The George Fisher Baker
Non-Resident Lectureship in Chemistry
At Cornell University

THE GEORGE FISHER BAKER
NON-RESIDENT LECTURESHIP IN CHEMISTRY
AT CORNELL UNIVERSITY

VOLUME 7

I

Spatial Arrangements of Atomic Systems and Optical Activity

II

Methods, Results and Problems of Precise Measurements at High Temperatures

III

The Constitution and Structure of Ultramarines

by

F. M. JAEGER

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UNIVERSITY OF GRONINGEN

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THIS BOOK I DEDICATE TO MY COLLEAGUES
AND MY AUDIENCE AT THE GEORGE FISHER
BAKER LABORATORY OF CHEMISTRY WITH
SINCERITY AND GRATITUDE

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PREFACE

The following lectures were delivered at Cornell University during the Second Semester of 1928–1929 under the George Fisher Baker Non-Resident Lectureship in Chemistry. They were originally written in English and rendered into their final shape by Dr. Cleveland Abbe, Jr., to whom I wish here to express my best thanks for the excellent way in which he has performed this task.

I shall be sincerely gratified if this book may prove to be a lasting reminder to my audience of my stay in Ithaca, during which I have had so much help from my colleagues at the Baker Laboratory and especially from Professor L. M. Dennis, who kindly gave me his advice and stimulation on many occasions. The splendidly equipped and organized Laboratory of Chemistry under his direction and the beautifully situated Cornell University will remain among the most pleasant of my recollections.

INTRODUCTORY LECTURE

The Present and Future State of Our Natural Resources

Almost nineteen years ago I set foot for the first time upon American soil, and it is most interesting, after so long a time, to now renew acquaintances with American life and American universities. Much has happened since my first visit to the United States, and the World War has in many ways revolutionized our ideas, whether for better or for worse. One American characteristic, however, has evidently not changed, and that is your cordial hospitality, which I find to be as warm today as it was twenty years ago.

I wish first of all to express my very sincere appreciation of the honor of the invitation to come to Cornell University as an incumbent of the George Fisher Baker Nonresident Lectureship in Chemistry, that splendid endowment which can not be too highly prized, because it affords your students what we in Europe regard as one of the most important features of university life, namely, frequent contacts with investigators from foreign countries and with workers in various branches of science.

It was with great pleasure that I accepted the invitation tendered to me by the trustees of this university and by Professor Dennis and his colleagues, and my earlier experience in America convinces me that my stay at Cornell will remain one of my most pleasant recollections.

It has become a custom for your guest to devote this introductory lecture to the presentation of some topic of general interest which is not necessarily related to his later technical lectures, and I have chosen for my subject this evening "The Present and Future State of Our Natural Resources."

This is a question of great general interest, and is one in which the chemistry of our day is deeply involved.

Archeologists have distinguished the different principal periods in the history of human civilization in a particular way, and have employed the terms the stone age, the copper and bronze ages, the iron age, etc., expressing in this manner their deep conviction that the state and future of the human race is, at every moment of its history, intrinsically connected with the special position in which man has been able to place himself with respect to his natural resources of materials and energy. This is true not only for the past, but equally so for our present-day world.

When we speak of "natural resources" in the most general sense of the word, we have in mind both the material and the energetic resources of nature. The first are represented by the more or less extensive stocks of materials of various kinds: coal, oil, iron, tin, ores of the heavier metals, many mineral and vegetable products, as potash, rubber, etc. Resources of energy, on the other hand, are certain natural stores that can be utilized directly for the production of mechanical force, or can easily be transformed into special forms of energy that can then be thus used. Waterfalls, the tides of the sea, and solar radiation are examples of such resources of energy. It is not always possible to draw a sharp line of demarcation between the two categories because "matter," as such, always represents also a certain stock of potential energy. Coal and oil, for instance, are only in small part utilized as raw materials; in by far the greater number of cases they are used as fuel, their energy of combustion being applied in our engines.

Let us now first consider the material resources. Everybody knows that our whole technical and industrial development depends upon the use of a certain number of indispensable raw materials. Technics and industry in their present aspect would be obliterated if the natural sources of supply of such metals as iron, copper, tin, lead, zinc, etc., should suddenly become completely exhausted. Dynamo and steam engine would in that case irrevocably disappear, just as the monsters of earlier geological epochs, the ichthyosaurus and the megatherium, vanished as soon as conditions became incompatible with their existence. Industry and traffic in their present form would become

quite impossible. And the same would be true if the stores of coal and oil were no longer at our disposal. Attention has repeatedly been drawn to the fact that the danger of such a catastrophe is not very remote if we continue to squander our capital of raw materials in the reckless way that has been pursued in the past and indeed is even now being followed.

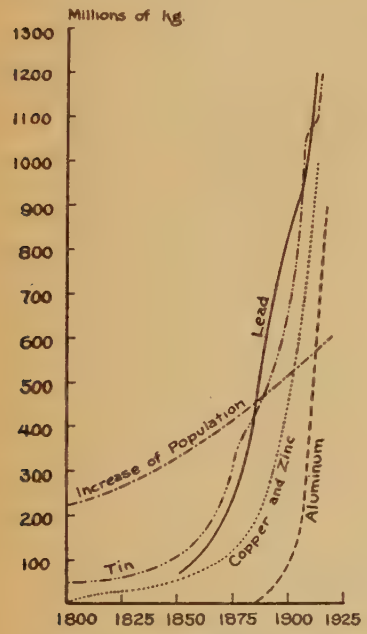


FIG. 1

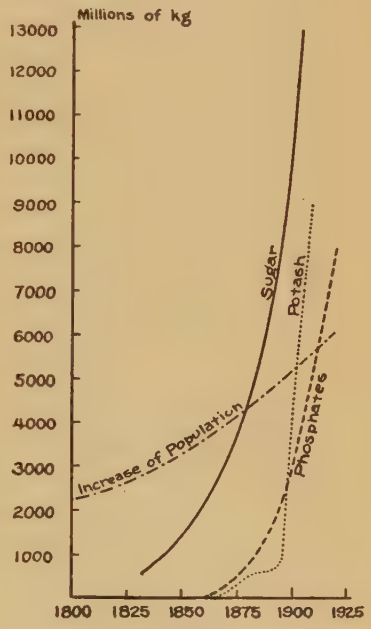


FIG. 2

Jeans has recently sharply emphasized the fact that humanity in its present stage of development must, properly speaking, be considered as only a "baby", if the still vast future existence of our race is taken into account—a baby, which hitherto has chiefly thought only of its nutrition and first physical growth, and which but recently has begun to look somewhat further than its immediate environment. We must, however, acknowledge that during this very insignificant portion of its whole presumable existence, that same baby has already shown that it is extremely gluttonous, because in only 120 years it

has fed on its natural resources in such an immoderate way as to cause anxiety concerning its future nourishment. All countries are now beginning to understand that the material resources of the world are by no means inexhaustible, and that it is urgently necessary to take measures to prevent further unrestrained destruction of them. Some numbers and graphs may help to elucidate the present situation.

In 1878 the annual world production of copper was 154 million kilograms; in 1892 it was 310 million; eight years later 713 million, and 1,413 million kilograms in 1917, about ten times the amount produced in 1878. Thus we see that the production of this metal has doubled about every nine years.

The annual world consumption of coal (Fig. 3) in 1840 was about 50 billion kilograms; in 1860 it was 200 billion; in 1880 it was 460 billion, and in 1920 it had increased to 1,550 billion kilograms, or thirty-three times the consumption in 1840.

In 1860 about 96 million liters of mineral oil were produced; in 1870 eleven times that amount; in 1880, sixty times, and in 1890 one hundred and fifty times that quantity. The present consumption has risen to the enormous figure of about 214 billion liters a year. The United States alone produces about three quarters of this tremendous quantity, and measures are now being taken to keep it stationary.

In the same period of sixty-eight years, the production of Chile saltpeter has increased to one hundred and thirty times the original quantity; it is now about three billion kilograms a year.

The three graphs will give you an idea of the general rates of increase of the yearly consumption of several important metals, coal, sugar, phosphates, potash, etc., and of the analogous form of the corresponding curves in all cases. In Figs. 1 and 2 there is also given a curve showing the increase of the world's white population. The striking difference between these two curves clearly shows that the yearly consumption of raw materials *per individual* has increased in quite an alarming way. In Figure 4 the curves

give a direct and impressive graphical representation of this increase of what I might call the present world's "individual hunger for raw materials."

Many authors have already often emphasized the fact that if this rate of consumption continues, the world demand will increase within a hundred years to such enormous quantities that it will far surpass the available amount of some of these materials, such as tin and oil.

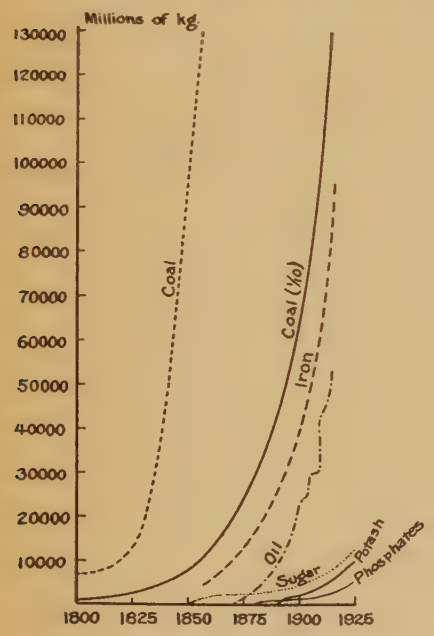


FIG. 3

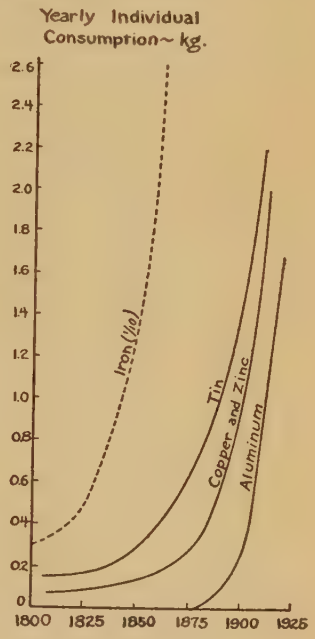


FIG. 4

Perhaps some of you might raise the objection that, according to one of the fundamental laws of chemistry, matter is indestructible and that the quantities produced must, therefore, continue to remain in circulation. But this law is not applicable to our economic life because great quantities of these materials are forever lost every year by "wastage," and thus are withdrawn from circulation in forms from which they are not recoverable. This is true, as everybody will immediately grasp, not only for such substances as coal and oil, which are completely destroyed,

but also for a great number of compounds of lead, zinc, tin and other metals, which, in the form of pigments or other chemical combinations, pass into the wastes of many industries and thus finally reach the sea. Very appreciable quantities of even the metals themselves are steadily lost beyond recovery.

As early as 1911 Sir William Ramsay, on the occasion of the meeting of the British Association for the Advancement of Science at Portsmouth, called attention to the fact that if English coal mining should go on at the rate of that moment, England, within 175 years, would no longer be able to provide herself with coal. B. W. Evermann in 1922, in an address before the American Association, gave a survey of the deplorable destruction of the forests of the United States, emphasizing the influence of it upon the water content of the rivers and on the change of the fauna in them. Several geologists are of the opinion that the stores of oil in the United States will, if consumed at the present rate, last no longer than forty or fifty years.

In 1921, upon the recommendation of the National Academy of Sciences, the American Association for the Advancement of Science and the National Research Council in this country, an Executive Committee on Natural Resources was created. This committee plans to make a continuous survey of the stocks of raw materials still present in America. All these facts clearly indicate that at last the conviction is more and more gaining ground that this vital question of supply needs to be kept constantly in view, and that we must give careful study to the methods by which the raw materials necessarily for our economic life may be rendered independent of the limited natural stocks accumulated during former geological epochs.

The answer to this question must principally be expected from scientific, and more particularly, from physical and chemical research. In this connection permit me to draw your attention to the enormously increased production and the simultaneous decrease in the consumption of coal in the blast-furnace industry, which was achieved only after long and painstaking systematic research of this and related processes in the laboratory; to the development of a

number of synthetic methods which now enable us to meet the alarming deficiency of those natural nitrates that are so indispensable for agriculture; to the gradual replacement of natural gasoline as a liquid motor fuel by synthetic alcohol and by "artificial" gasoline, the production of which in 1928 by the Farben Industrie of Germany alone amounted to one hundred million kilograms a year, while for 1929 it is estimated that the quantity will be doubled. The problem of the most economical way of using coal in industry and as a fuel, is being studied on all sides in a number of laboratories specially equipped for that purpose. New possibilities, be it by the improvement of existing methods or by the development of completely new ones, are created every year in scientific and industrial laboratories. Numerous tests are continually being made as to the possibility of replacing many raw materials, hitherto considered indispensable, by others which will do as well or even better than the old ones. Thus, for instance, the use of metallic aluminum and its alloys for constructive purposes, instead of the often more costly heavier metals, has increased very rapidly during recent years. In industry, and to a certain extent also in our daily life, measures are now taken to avoid the dissipation of raw materials by making use, in an appropriate way, of waste products formerly considered as valueless. It is worth remarking that an undeniable change of direction can be seen in the choice of raw materials for all kinds of purposes. The effect of this change is that the heavier metals, which, in general, are obtained by mining at the lower levels of the earth's crust, are being replaced by the less dense metals and other elements that are present in the upper layers of the lithosphere, and which, therefore, may with much less cost be obtained by surface mining. Among those elements silicon which in the form of silica represents 60 per cent, and aluminum, which as its oxide and as other compounds represents about 15 per cent of the earth's crust, are, with calcium and magnesium, the most predominant ones. I have already mentioned the enormous yearly increase in the application of aluminum. Recently an alloy of this metal with silicon, termed "silumin," has been brought

upon the market for construction purposes, and is replacing iron in many cases. In this connection let me further draw your attention to the fact that the use of concrete and Portland cement, for the same purposes, is increasing yearly at a gigantic rate, and that glass and other compounds of silica are now used in many cases where formerly metals were employed. That this change of direction necessitates the solution of many totally new chemical problems need hardly be emphasized. Let me only remind you here of the possibility of extracting metallic aluminum, not from bauxite but from the various kinds of ordinary clay which are everywhere immediately at hand on the earth's surface and, therefore, represent a much cheaper material.

Thus, it is again the quiet research work of the chemist in his laboratory, the results of which do not always seem to lead immediately to practical applications, which in the end prepares the fertile soil from which we shall be able to reap the technical and industrial victories of the future. As Lord Cecil remarked some years ago, it is principally by new conquests of nature that our society can gradually reach a higher level of life. Indeed, at the present time, as Sir William Bragg recently emphasized in his address to the British Association in Glasgow, industry is the slave of pure scientific research rather than its master. Every far-seeing government must set itself the task of supporting this scientific investigation by abundant endowments, because only new discoveries and their applications will be able to avert from mankind the ominous menace of an early shortage of our material resources, and the consequent impoverishment of our civilization.

Let us now consider the second category of natural resources, the energetic ones.

It is a well-known fact, that, both for the biological processes in plants and animals as well as for the maintenance of human civilization, a continuous import of energy from outer space to our planet is necessary. The only source of energy that practically needs to be taken into account in this respect, and which daily furnishes enormous

quantities of energy, is our sun. In whatever form we meet with energy on the earth, whether it be stored in coal or oil or be immediately available to us, as in the flowing or falling water or in the winds, it can in all cases easily be understood that this energy has always its real origin in that of the radiation which the sun continuously emits in all directions into space. If this radiation is absorbed, it will for the greater part be transformed into heat, which causes the water on the earth to evaporate, and thus gives rise to the mighty formation of clouds. Inversely, the condensation of this water vapor is the cause of rain and snow fall, which in their turn feed the rivers, seas and waterfalls. The differences in temperature and pressure in the earth's atmosphere that are brought about under the influence of the solar radiation are the cause of air currents which give rise to the energy of the wind. The radiant energy of the sun given out several hundreds of millions of years ago is now stored up in the form of chemical energy in coal, after having been transformed and accumulated in the living vegetable cells of those far-off eras. Through the process of combustion, this stored-up chemical energy is used by us in our steam engines and gas motors of today. This stock of coal, and also of mineral oil, nowadays represents the principal source of energy that man utilizes for the production of mechanical power. There is no other source of energy on the earth the output of which can even distantly be compared with that derived from the two sources just mentioned. We can safely say that practically our whole need of energy is supplied by that fossil stock of solar energy which is at present stored in our deposits of coal and oil. The necessary consequence of this is that we draw upon our energy capital to so great an extent that it must finally become exhausted, unless some way be found to replenish it by again accumulating this mighty solar radiation against the day when our stores of coal and oil will have been exhausted. The total quantity of coal on the earth seems not to exceed about 2,000 billion tons, of which at the present time about 1.5 billion tons are used annually. This yearly consumption, however, is increasing so rapidly that our coal deposits will hardly be sufficient

for another thousand years, a period that is very short in comparison with the length of the future existence of mankind on the earth. But the exploitation of the coal deposits that still remain will become impossible long before that time, both for technical and for economic reasons. Within a period much shorter than these thousand years, the ominous consequences of the present reckless demolition of our coal fields will make themselves seriously felt, for the simple reason that the coal must be extracted from ever deeper and deeper levels with consequent rapid increase of the cost of mining.

The question as to whether it then will be possible to obtain the indispensable energy from other sources on earth must, so far as can now be judged, be answered in the negative. Again at the instigation of Sir William Ramsay, the possibility of such an eventual development of other energy sources was seriously investigated in 1910 in England by a number of competent men. On that occasion the possibilities were taken into account, of making use of the ocean tides, of the internal heat of the earth, of the energy of the winds and of waterfalls, of the kinetic energy of the earth's rotation and its yearly motion in space, of the chemical energy of wood and peat supplies, and finally of the intra-atomic energy of the atoms of the elements.

This official inquiry showed that the application of the internal heat of the earth, of the kinetic energy of the earth's motions, of the energy of the winds, and the use of wood and peat supplies, never would be of any significance for the solution of the problem in comparison to the enormous quantities of energy yearly furnished by our resources of coal and oil. The energy that could be obtained by the disruption of the atoms of our chemical elements would be enormous in amount, but we need not further consider it at this time because in the opinion of our ablest scientists the practical accomplishment of this objective will be achieved only in the far distant future, if ever.

The available water power on the earth would, according to Engler, amount to about the energy of seventy million tons of coal annually, *i.e.* to about 4 per cent of the

energy necessary every year. Of course, the total water power present on earth is much greater, but an appreciable part of it will probably never be available. A calculation made in 1922 by Steinmetz, seemed to indicate that the energy of the flowing water, corresponding to the yearly amount of rain in this country, would be almost equivalent to that of your yearly coal consumption. Spoehr, however, has emphasized that these calculations are wholly theoretical, as a great part of that energy is inaccessible and the distribution of the remaining energy over such an extensive territory would meet with almost insurmountable difficulties. Therefore, in this respect America is, for the time being, dependent in a large degree upon her own resources of coal and oil, of which the latter seems to be rapidly approaching final exhaustion, notwithstanding the apparently reassuring fact that new sources of limited extent are frequently being developed.

The possible use of the tides of the sea has occupied the attention of various inventors since the fifteenth century. Indeed, the periodically alternating low and high ocean tides would furnish gigantic quantities of energy if it were only possible to use them for mechanical purposes in a not too expensive and complicated way. In recent times several solutions of this problem have been proposed, some of which have already found a practical application, although only on a relatively small scale, in France, in England and in several places in Germany (Ditmarschen, Husum, Hüll). The systems with two large communicating water reservoirs, instead of those with a single one, seem to be preferable as they allow an uninterrupted action both day and night, even during neap tide. Their theoretical efficiency, for a difference in sea level of about three meters, is, however, less than that of a system with a single tank, and is not greater than about 4,800 kilowatts for each tide and for each square kilometer of surface of the reservoirs. In practice this efficiency is appreciably diminished by a number of uncontrollable factors, as, for example, the irregularities in the level-differences of the tides, to the square of which the energy output is proportional. Such a plant would be extremely expensive

and its maintenance would be very costly. Consequently it could be operated economically only under very favorable local conditions. It is therefore probable that no satisfactory solution of the problem of the production of energy in this manner is to be expected.

Recently, however, there seems to be indicated another way of deriving energy from the sea, which, in my opinion, may become of high significance in the future. I refer to the experiments of G. Claude and P. Boucherot upon the utilization of the relatively small but very constant temperature-differences that exist throughout the year between the sun-heated surface of the tropical oceans and their deeper layers, the temperature of which is kept at from 4° to 5°C by the cold polar currents. In 1913 your countryman Campbell pointed to the possibility of obtaining mechanical or electrical energy by means of these very constant temperature-differences, and in 1923 Romagnoli, Dornig and Boggia made analogous propositions. It was, however, only recently that the well-known French chemist Claude and his collaborator Boucherot succeeded in giving experimental proof of that possibility. They were able to demonstrate that a small Laval turbine designed to be driven by steam within pressure limits ranging from 20 to 0.2 of an atmosphere, can advantageously be driven by water vapor at pressures between only 0.04 and 0.01 of an atmosphere, corresponding to temperature-differences between 25° and 8°C only. According to their calculations and experiments, a net output of 54,000 kilogram-meters could be obtained from each cubic meter of water between 28° and 5° if there be subtracted the energy that is necessary for pumping the cold and air-free water from the depth of the ocean to its surface. An installation of this kind having a capacity that effects the transfer of 1,000 cubic meters of cold water every second, would be able to produce 400,000 kilowatts of electrical energy, this efficiency being about thirty or thirty-five times as great as that of a low-and-high-tide plant of the same dimensions. In their provisional installation at Ougree-Marihaye, Claude and Boucherot recently demonstrated before a meeting of en-

gineers that a turbine could be run by utilizing the slight temperature-differences of the water of the Meuse, ranging only from 28° to 8°, and that it could drive a dynamo with a capacity of fifty-nine kilowatts. The calculation by Boucherot of the necessary costs of installation, seem undeniably to indicate that the practical realization of this idea lies very probably within the limits of technical possibilities.

The question as to whether it would be possible to use our present stocks of coal and oil in a more economical way than is now usually employed, is of high importance and has often been the subject of discussion and investigation. In the present exploitation of our oil fields, about three-fourths of the oil remains in the soil. This needs, in the future, to be recovered by some process suitable to the purpose. Even the continuous improvement of the steam engine, or its replacement by turbine or gas motor, can not eliminate the ominous fact that the greater part of the heat of combustion of the coal and oil will, when thus used, always be wasted. At the present time it seems that the most effective way of limiting, as far as possible, this squandering of energy consists in the combustion of the coal *in loco*, *i.e.* at the mines themselves, and the immediate utilization of the heat of combustion for the production of high-tension electric currents. It is possible that some way may be found for transforming the potential energy of the coal directly into electrical energy, but experiments along this line have not yet met with practical success. None of the so-called "fuel batteries" constructed for this purpose in the last decade can be considered as being adapted to practical development, because their current efficiency, even at higher temperatures, remains in each case much too small by reason of the unsatisfactory reaction-velocity of the electrochemical processes going on in them.

As the matter now stands we can say that, in answering the question as to how to make the future necessary energy-production most completely independent of the stocks of fossil energy accumulated in former geological periods, we are chiefly confined to the mighty current of

radiant energy that is flowing to us directly and continuously from the sun. This quantity of radiant energy appears to be stupendously great, but it is now almost completely lost by dissipation.

According to Langley's measurements of the solar constant, each square meter of the earth's surface receives, every hour, a quantity of radiant energy that is equivalent to 1,800 calories. If we regard the sun as limiting himself to an eight-hour working day in tropical regions, it can be calculated that every square meter of the earth's surface daily receives from the sun's radiation a quantity of energy equivalent to the heat of combustion of 1.3 kilograms of coal. For every square kilometer this is equivalent to 1,300,000 kilograms of coal, which means that the total annual amount of energy produced throughout the world, through the consumption of coal, would be equaled by the radiant energy of the sun which, during a like period, falls upon a surface of only 3,300 square kilometers (1,275 square miles). The desert of Sahara has a surface of about six million square kilometers (2.3 million square miles), and therefore annually receives a quantity of solar energy that is equivalent to more than 1,800 times that derived from the world's total yearly consumption of coal.

At present this enormous quantity of energy is almost completely lost; only 1/300 of it is absorbed and used by the living plants on the earth. Although this percentage is a very small one, the total quantity of radiant energy annually absorbed in this way over the whole land surface of the earth still amounts to about fifteen times the yearly world consumption of coal. But the question arises as to whether and in what way it would be possible to catch the enormous quantity of solar energy that now is dissipated every year, and to apply it to the production of mechanical and electrical energy.

In the consideration of this question two points should be emphasized at the outset: first, the necessity of concentrating and accumulating the solar energy supplied to large surfaces; and second, of absorbing this solar energy to the greatest possible extent. Absorption must precede the transformation of radiant energy into those other forms

in which it can be used for our immediate purposes. After absorption, the solar energy may be immediately transformed into heat which may then be utilized in the usual manner for the production of mechanical work, or the radiant energy may be absorbed by special substances in which it sets up a "photochemical" reaction and thereby produces a certain amount of chemical energy. This chemical energy can afterwards be changed into another form of energy suitable for our use. Nature has solved the latter problem, of utilizing the solar energy, through a most remarkable photochemical process in which that mysterious laboratory which we call the "living vegetable cell" is involved. The plant utilizes the radiant energy of the sun to synthesize a large number of complicated chemical substances in its protoplasm. These compounds accumulate in the plant organism, and their stored chemical energy can later be employed for the production of mechanical work. We also know of other photochemical reactions in which a fraction of the absorbed radiant energy is immediately transformed into electrical energy. I will discuss these more fully later on.

Let us first consider the other and simpler case of utilizing the solar energy by first concentrating and absorbing it, and then transforming it into heat.

Concentration of the radiant energy may be effected either by means of large lenses or by a system of mirrors; the absorbent heat-reservoir is placed at the focus. In actual practice, only systems of mirrors have been used. These are mounted on a light frame which permits them to be easily rotated, which is, of course, necessary because they must follow the apparent motion of the sun in the sky. The radiant energy concentrated by these mirrors falls upon a metallic reservoir which is blackened on the outside and which contains some volatile liquid having a considerable vapor pressure at relatively low temperatures. Ammonia, sulphur dioxide or certain organic liquids of low boiling point are employed. An example of this type of installation is that devised by Schulz, in which, using sulphur dioxide, an output of about 1 H. P. was obtained for each square meter of surface of the absorbent reservoir.

At the Ostrich Farm in Pasadena they have used, and perhaps they still are using, a conical aggregate of mirrors of ten meters diameter, in the focal line of which a steam boiler was placed. This developed steam at a pressure of from ten to fifteen atmospheres after only one hour's exposure to the sun, and the device was used for pumping water at the rate of 6,000 liters per minute, and for driving a dynamo.

It may be possible that in dry and tropical climates this method of utilizing solar energy will be successful on a small scale, the cost of the equipment being compensated by the fact that the expense of operation is very low. But under less favorable conditions this device can never be expected to yield a satisfactory solution of the problem, because it concentrates the radiant energy that falls on only relatively small surfaces. The proposal of Claude and Boucherot offers much greater promise in this respect, because it utilizes the energy that is accumulated over the immense surface of the ocean during long intervals of time.

These considerations lead us to the conviction that the final solution of the problem must be sought rather in the utilization of specific photochemical reactions of the radiant energy. I intentionally use the word 'specific' here because experience has shown us that the action of radiation upon chemical substances is highly exclusive in character. The assimilation of carbon dioxide by plants is a well-known example. The radiation is here absolutely necessary for bringing about this reaction which goes on at ordinary temperatures, the living cell being able under the influence of sunlight and with the aid of its chlorophyll to synthesize a number of complicated substances which we in the laboratory, in spite of the high development of synthetic chemistry at the present time, are able to produce either not at all or only with great difficulty, even when high temperatures and powerful agents are employed.

We are still dependent, for the production of most of our foods and drugs, upon photochemical processes that proceed under the influence of solar radiation in the plant cells. Although it seems possible, according to the experi-

ments of Ciamician and Ravenna, to influence these processes within certain limits by special external stimuli, we really as yet have little understanding of the true mechanism of these reactions. The researches of Baly have shown that moist carbon dioxide may, in the presence of certain substances such as compounds of cobalt or nickel, be transformed through the influence of ultraviolet light into substances like sugar. He may be considered to have demonstrated that it is possible to produce, in the laboratory, compounds that are formed by the natural processes of the living plant. No one, as yet, has succeeded in carrying on this photochemical synthesis on a large scale. It offers, however, an alluring prospect because, according to Brown's investigations, if it is assumed that a quantity of solar energy equivalent to five calories will transform one liter of carbon dioxide into sugar, and if only 4 per cent of solar energy during an eight-hour day is assumed to be photochemically active, it would be possible in this manner to produce 170 kilograms (374 pounds) of sugar every day by the use of a tank having a surface of only 1,000 square meters (about one hundred feet square). This amount of sugar, besides its value as nutriment, would, if used as a fuel, be equivalent to about seventy-five kilograms of coal. It is extremely doubtful, however, whether this method of utilizing solar energy will ever be brought to practical success.

The remaining possible solution of the problem of utilizing the radiant energy of the sun for the production of mechanical work, is the application of reversible photochemical reactions which proceed in such a manner that the absorbed radiant energy may be converted into a usable form such as electrical energy. If the reversibility of such photochemical reactions is nearly quantitative in character, the photosensitive system of substances will then, in respect to solar radiation, play a rôle analogous to that of the lead storage battery with respect to electric energy. We might term such instruments "radiation accumulators;" they would be exposed during the day to the solar radiation which would cause a certain photochemical reaction, and then at night when left in the dark this reaction

would reverse, the materials would return to their original condition, and the radiant energy absorbed during the day would be set free and stored up for mechanical uses.

It has long been known that such reversible photochemical processes really exist. For example, if a water solution of mercuric chloride and ferrous chloride is exposed to light radiation, a reaction takes place in which certain amounts of mercurous chloride and ferric chloride are formed, a chemical equilibrium between the four salts being finally reached. If, now, the solution is placed in the dark, the substances will revert to their original form and during this inverse reaction the radiant energy absorbed will be completely set free in the form of electrical energy. It is possible to obtain a tension of 0.17 volt by means of such a photochemical cell; consequently a dozen such cells joined in series will yield the current furnished by an ordinary lead storage battery.

Again, such a photochemical cell can be made by placing two platinum electrodes in an acidulated solution that contains potassium iodide and ferric chloride. When this cell stands in the dark, ferrous chloride and a certain amount of free iodine will be formed, the iodine remaining dissolved in the excess of potassium iodide. On exposing this cell to the action of light, the chemical equilibrium is displaced in the opposite direction, and potassium iodide and ferric chloride are regenerated. As with the previous cell the absorbed radiant energy is set free as electric energy.

Another remarkable example of a phenomenon of this nature is described by Rigollot. Two plates of red copper, each of them superficially covered with a thin layer of cuprous oxide, are placed in a saturated solution of sodium chloride. If now one of these plates is exposed to light radiation and the other is kept in the dark, an electric current passes through the wire that connects the two electrodes. This current continues as long as the exposure lasts. The whole system returns to its original state in the dark. If the other electrode is illuminated, the electric current produced in the circuit flows in the opposite direction.

These various experiments furnish definite proof that it is possible to convert radiant energy into electrical energy, by means of reversible photochemical processes.

There is, however, one great drawback to the practical application of such a method, and that is the very low intensity of the electrical current that is produced. The electrical work that can be done, a product of the voltage and current intensity, is, therefore, in all cases only extremely small. The explanation lies in the fact that the reversible transformations which take place in these cells, are characterized by very small reaction velocities, and consequently the energy that is carried off can not be resupplied by the photochemical reactions with sufficient rapidity. The photochemical effect appears, in general, to be the strongest in those cases of reversible processes in which the oppositely directed reactions are slowest, and because of this fact, some investigators are inclined to doubt whether the utilization of such radiation accumulators can ever be of practical value. This opinion may, however, prove to be unduly pessimistic. The construction of such cells is wholly a problem of reaction kinetics. If it should prove possible to devise radiation accumulators or voltaic cells in which reversible and very rapid photochemical changes take place when radiation of such wavelengths as are contained within the solar spectrum is employed, the problem of using solar radiation as a source of energy might be regarded as definitely solved.

We are, however, still far distant from this goal. Photochemistry is still in its infancy and it has not yet outgrown the stage of mere empiricism. It is quite possible, however, that when man's existence becomes seriously menaced because of a shortage of energy, photochemistry will rescue him from his distress.

The protection of mankind from this danger rests chiefly upon the physicist and the chemist, and they must ever be on the alert to find solutions for these intricate problems that involve the very existence of our race.

PART I

SPATIAL ARRANGEMENTS OF ATOMIC SYSTEMS AND OPTICAL ACTIVITY

CHAPTER I

The Elements of Symmetrical Figures

In this series of lectures I propose to survey our modern views concerning relations between certain geometrical and physico-chemical properties of atomic systems, as they appear in the molecules of inorganic and organic substances. I shall also discuss a number of the results already obtained in the many efforts to test experimentally the underlying principles. When referring to the stereo-chemical pecularities of such atomic structures it will often be necessary to employ geometrical considerations and relationships of a very general character which appear to hold for all more or less regular tridimensional arrangements. These are usually summed up in the mathematical theory called the "general doctrine of symmetry." Its fundamental significance for our problems, as well as for many other questions in physics, crystallography, and the like, is now universally recognized. We must, therefore, first devote some attention to its principles and the next few lectures will be devoted to their exposition. The brief time at my disposal will not permit lengthy consideration of this very extensive field of theoretical research. Therefore, I shall give, as it were, a bird's eye view of the whole field and devote most of my time to the more imperative subjects. The necessary theoretical considerations will be made as generally understandable as possible and the more rigorous mathematical reasonings will be avoided. Those who wish to follow the subject in more detail will find the references to the current literature helpful.

A consideration of the geometrical forms about us reveals that many of them are quite lacking in regularity, for example, the hand, the foot, a scalene triangle. Other figures, however, appear to have a more or less regular structure. Thus they may consist of several identical parts

repeated at regular intervals around an axis, as are the colored petals of the corolla of many flowers, the parts of such lower animals as the starfish and sea-nettle. When we consider the human body as a whole, also many leaf forms, we see two halves equally arranged with reference to a single plane. Sometimes other figures show a repetition of their component parts according to the first or the second way simultaneously, as is seen in the familiar cells of the honeycomb or the beautiful forms of crystals, or the siliceous and calcareous skeletons of the radiolariae and the corals. Such objects are called symmetrical in contrast to those lacking in regularity which are called unsymmetrical. Symmetry therefore always implies a regular repetition in space regarding certain identical, or at least analogously constructed, parts of the object. For example, if a perfectly arbitrary irregular arrangement of dots, as shown in Figure 5, is repeated regularly by turning it about an axis through angles of 72°, 2 x 72°, and so on, the resulting figure will have quite another aspect (Figure 6a) than the original pattern.[1] The latter has now become a symmetrical figure making an ob-

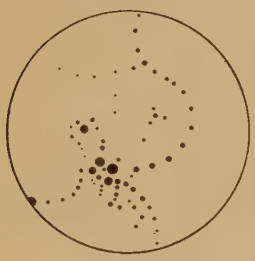


FIG. 5

[1] The remarkable fact, that the mere regular repetition of a visual impression—even if this be originally only an indifferent one—has an undeniable aesthetic effect upon the observer, is explained by the intensification of the primary impression by its repetition, in connection with or combined with the fact that the observer involuntarily expected this result from his idea of the special mode of repetition. The symmetrical arrangement is one of the ways in which mental action is facilitated. It is a question of adaptation of attention to subsequent observation as a consequence of the psychological preparedness for a coming impression, when its special nature is on the same or a comparable level with that anticipated by the imagination. A feeling of comfort and delight will be produced because of the easy assimilation of the real occurrence to the analogous expectation already present in the observer's mind. This is similar to the feeling of delight that always accompanies the relaxation of a mental tension.

The primary impression need not be repeated in such a manner that the repeated impressions are absolutely identical with the original, it is sufficient if they are only highly analogous. Thus they may be only conformable, but increasing or diminishing consecutively to the same extent or in the same ratio. Thus the shells of *Nautilus pompilius* (Fig. 7) with their series of gradually increasing chambers also make an aesthetic impression. In such cases the repetition becomes more a matter of rhythm. The somewhat tiring and chilling action of rigorous symmetry is recognized by modern architects, and the effect is often mitigated by substituting a mere rhythmic repetition of conformable parts of different dimensions. The structure of musical works, such as sonatas and symphonies, show analogous character, the same is true of the dance where subsequent repetitions are combined with a slight modification or modulation of movement.

vious aesthetic impression. The axis about which the original pattern is now arranged is called an axis of symmetry of the final figure. If the symmetrical figure possesses a finite number of such repetitions—and in future we shall always have to deal with such figures—it is evident that the smallest angle of rotation α through which the figure must be turned to make it coincide with itself and which, therefore, is characteristic of the symmetry peculiar to the whole figure, must always be commensurable with a complete rotation. Thus, α will be equal to $2\pi/n$, where n is a whole

FIG. 6a

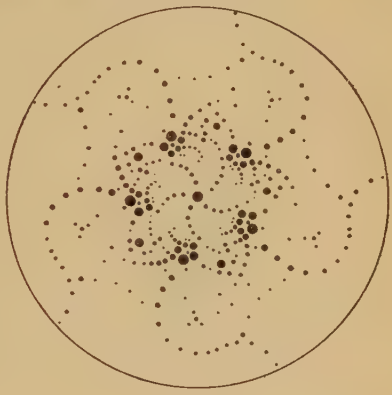


FIG. 6b

number and usually a small one. This smallest angle α determines the period of the symmetry axis, and the number n its valency.

For example, if α equals 120°, the axis is a ternary axis A_3; if α equals 60° the symmetry axis is a senary one, A_6. When the axis is A_∞ it is called an "axis of isotropy" and plays an important rôle in many physical phenomena. When α is equal to 360°, n equals one, the figure shows mere identity with itself and, in common language, is called asymmetrical. Those figures having no other symmetry elements than axes of symmetry are said to have mere axial symmetry.

As has already been pointed out, no axes are present in the case of many leaves, of the human body, and similar figures. If we imagine the human body to be reflected in a vertical mirror passing through the middle of the body,

the resulting mirror image exactly coincides with the body itself in its original position. The right and left halves in the mirror are not identical in this case. They are each other's mirror images and it is impossible to make them coincide with one another by any change in position be it a shift or a rotation. In the same way it is impossible to use a left-handed glove on the right hand or vice versa. We are accustomed to say that the human body is a symmetrical figure only with respect to a mirror plane or symmetry plane; either half considered separately is different from its mirror image, just as the right and the left hands differ from each other. Such parts or figures, differing from their mirror image, are called enantiomorphous. The fact that the body as a whole is identical with its mirror image, is due to the particular circumstances that its symmetry element is a symmetry plane; its separate halves, however, are enantiomorphous because they lack such a symmetry plane.

FIG. 7

We see, therefore, that symmetrical figures can be brought to coincide with themselves in other ways than by rotating about an axis; many of them must be reflected in mirror planes to do so.

A figure may be transformed into its mirror image in yet another way than by reflection in a plane. If such a figure as the irregular tetrahedron ABCD of Figure 8 is given, and straight lines are drawn from each point of the figure through the point P in such a way that on each line a length PA′, PB′, etc., is cut off so that PA′ equals PA, PB′ equals PB, etc., then the points A′, B′, C′, D′, taken together will determine a figure A′B′C′D′, which is the mirror image of ABCD. This process is called "inversion." The point P is called an inversion center and may be placed anywhere, even within ABCD. If ABCD is equal to A′B′-C′D′, then P is a symmetry element of ABCD and is a symmetry center. Figures possessing such a symmetry center are identical with their mirror images, as well as when they possess a symmetry plane.

We have seen that the symmetry elements of a regularly formed figure are axes of rotation in the case of axial symmetry, and symmetry planes or a symmetry center in the case of figures coinciding with their mirror images. We must here emphasize the fact that the two latter are not the most general types of symmetry elements and therefore they are not adequate to describe the symmetry of all possible regular figures that are identical with their mirror images. An example will make this clear. Suppose the primary pattern of a composite symmetrical arrangement, which therefore can be regarded as generated

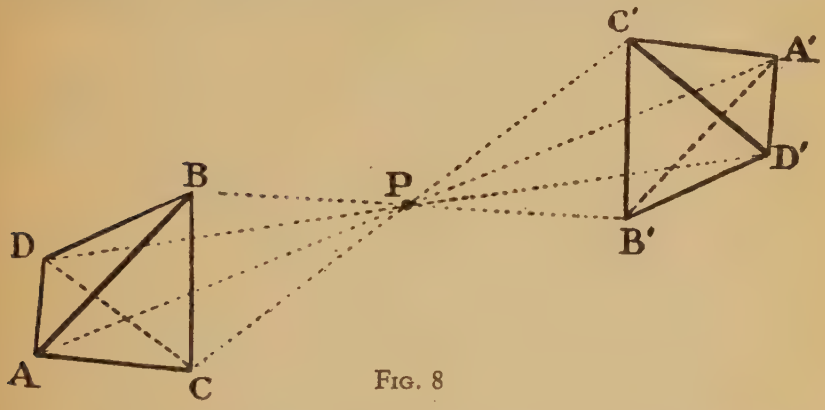


FIG. 8

from it by some process of regular repetition, be quite lacking in any symmetry element or to possess mere axial symmetry so that in every case it is distinctly different from its mirror image. As a concrete example consider the irregular tetrahedral design of Figure 9, ABCD. If we turn this tetrahedron through angles of 90°, $2 \times 90°$, $3 \times 90°$, $4 \times 90°$, consecutively, about the axis LL′, but in such a manner that each rotation about the axis brings with it a transformation of the pattern into its enantiomorph at each new position, so that after each turn it may be considered as reflected by a plane mirror perpendicular to the axis L L′, then we shall obtain a very special kind of symmetry of the figure as a whole. Thus after turning ABCD through 90° we obtain its inverse form A′B′C′D′; in turn A′B′C′D′ is rotated 90° becoming inverted in its new position into A″B″C″D″; and so on. Having completed a rotation

of four times 90° and a corresponding number of inversions, it is finally reduced to ABCD in exactly the same position whence it started. The whole complex of tetrahedral parts thus obtained is that figure in space whose symmetry we wish to describe: it consists of two tetrahedra ABCD and A″B″C″D″, which are mutually opposite and congruent, being rotated through 180° with respect to each other; and of two inverted tetrahedra A′B′C′D′ and A‴B‴C‴D‴ also mutually opposite and turned through 180° with

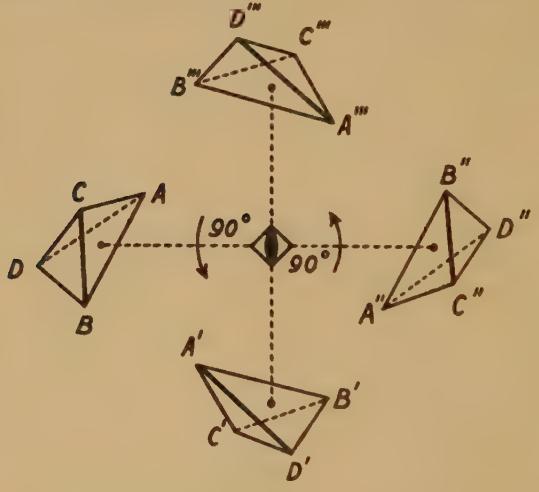


FIG. 9

respect to each other. The straight line joining ABCD and A″B″C″D″ intersects at a right angle the corresponding line joining A′B′C′D′ with A‴B‴C‴D‴.

By reflection in an arbitrarily placed mirror the whole figure may readily be proved to be coincident with its mirror image, just as the human body was. But this figure now possesses no plane of symmetry nor any symmetry center, so that its symmetry cannot be described with the aid of any of the symmetry elements so far considered. As an axis of rotation LL′ is not even a quaternary axis, as it should be since α equals $2\pi/4$; in fact this is not higher than a binary symmetry axis. In order to describe the special symmetry of the configuration before us it is necessary to introduce a new symmetry element character-

ized by exactly the same process of transformation that is followed in securing the above configuration. An axis such as LL′ is called a mirror-axis, an axis of the second order, or an axis of alternating symmetry. It has a definite period, α equals $2\pi/n$, exactly as the ordinary axes of rotation have; here also the value of n is characteristic of the special properties of the axis so that the possibility of replacing the axis LL′ in some cases, for example, by a combination of other symmetry elements, depends wholly on the value

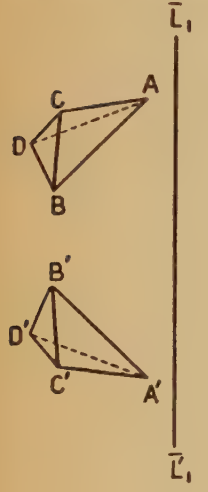


FIG. 10a

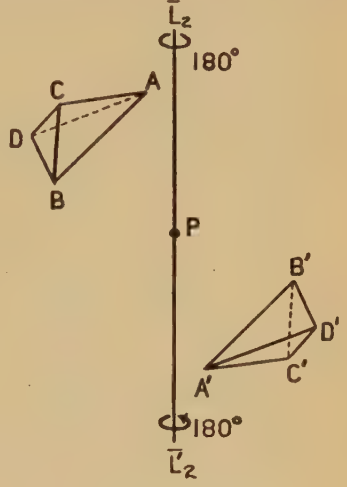


FIG. 10b

of n. In our case LL′ is a quaternary mirror-axis and the symmetry of the present figure can be described in no other way. But this need not always be the case. The mirror-axis is the most universal type of symmetry elements for figures that coincide with their mirror images. It can be easily demonstrated, however, that the other symmetry elements, such as the symmetry plane and the symmetry center, are but special cases of the mirror-axis. If n equals 2 this binary mirror-axis (Figure 10b) transforms ABCD into its mirror image A′B′C′D′, both patterns being so situated with respect to each other that the whole operation is equivalent to an inversion with respect to a certain point P lying in LL′, so that the whole figure possesses a symmetry center. If n equals 1, ABCD and its mirror image A′B′C′D′

will be so situated that they are in juxtaposition with respect to a plane perpendicular to LL′ and the whole figure therefore has a single plane of symmetry (Figure 10a). The symmetry plane is therefore simply a unary mirror-axis, the symmetry center a binary mirror-axis.

In the same way it may be readily proved that for all odd values of n the mirror-axis, $\overline{A}_n$, can be replaced by the combination of an ordinary symmetry axis, A_n, of the same period, with a true symmetry plane perpendicular to it. If n is an even number, however, two cases must be distinguished according as n/2 is odd or even. If n/2 is odd the axis A_n may be replaced by an ordinary symmetry axis with a period of α equal to $2\pi/\frac{1}{2}n$ which is equal to $4\pi/n$, combined with a center of symmetry located on that axis. If n/2 is an even number, that is, if n is divisible by 4, then the mirror-axis LL′ can never be replaced by any other symmetry element.

The preceding considerations of the special symmetry of spatial configurations will suffice for our present purpose. More rigorous treatment of the whole subject may be found in my *Lectures on the Principle of Symmetry and its Applications*, where full references to the literature will be found.[1] The results discussed above may be summarized as follows:

A. Symmetrical configurations in space have the property that they can be brought to coincide with themselves in more than one way. Some figures are identical with their mirror images, some differ from the same. They are produced by certain regular repetitions of subordinate parts or patterns which are either identical or related to each other as right and left hands are.

B. Certain symmetrical configurations have their symmetry fully described as rotations about a symmetry axis with a period $\alpha = 2\pi/n$, where n is a whole number. Such configurations are said to be axially symmetrical. They always differ from their mirror images, that is, they can always exist in two forms so related to each other as right

[1] F. M. Jaeger, *Lectures on the Principle of Symmetry and Its Applications in All Natural Sciences*. 2d ed. (Amsterdam, 1920; French transl. Paris, 1926.) See also: *Scientia*, p. 379 (1923); *Chem. Weekblad*, 19, 510 (1922).

and left hands are and which are called enantiomorphous. Such enantiomorphous configurations can never be made to coincide with each other simply by rotation or some other motion alone.

C. There are configurations in space which are identical with their own mirror images. The necessary and sole condition for this is that these configurations possess symmetry axes of the second order (mirror-axes) or as special cases of these, symmetry planes or a symmetry center. Of course, figures can simultaneously possess symmetry elements of the first order; but even so, the presence of a single symmetry element of the second order makes them identical with their mirror images. Some mirror-axes may be replaced by a combination of other symmetry elements, but this appears to be impossible if n is divisible by 4.

As we are now familiar with the true nature of symmetry elements necessary to describe the special properties of symmetrical figures, we now can attack the problem of deducing all possible types of symmetry that arrangements in space can possibly present. These are found in the finite figures we call chemical molecules and in the non-delimited atomic systems of crystalline matter. A number of mathematicians of the 19th and 20th centuries have now completely solved this problem. What made the solution possible is the fundamental fact that different symmetry properties cannot be combined in a wholly arbitrary manner in the same figure, because the simultaneous presence of two symmetry properties necessarily involves a third symmetry property, and so on. In the simple case of a combination of two ordinary symmetry axes having periods α and β, this fact immediately becomes evident, because every two rotations about different axes always produce a third rotation about another axis whose direction and period γ may be found by one of Euler's well-known constructions. Further, if we have simultaneously present a symmetry axis A_p, of period number p, and another A_q with a period number q, it must be clear that reasons of symmetry require there shall be p other axes of the type A_q placed about A_p, and in the same way q axes of the type

A_p placed about A_q; etc. The symmetry properties of such a figure not only make the whole figure coincide with itself, but also its complete system of symmetry elements with itself. What is true for axes of rotation holds also for axes of the second order that may be present. Thus there are a number of rigorous mathematical relations between all symmetry elements of a symmetrical figure; therefore each combination of symmetry elements must always fulfill special conditions imposed by the mathematical relations. Owing to this special circumstance, the problem of deducing all possible types of symmetry is a quite definite one and its solution merely a matter of pure mathematical reasoning.

It is a remarkable fact that although the period number n of the symmetry axes theoretically may have any value between 1 and ∞, and the number of individual symmetry groups therefore is also infinitely great, the number of principal different "types" of symmetrical figures in tridimensional space appears to be a rather small one. It is unnecessary, however, to dwell upon this fact in this place.

CHAPTER II

Pasteur's Law; Asymmetric Atoms.

In Chapter I we learned the general conditions that must be satisfied if configurations in tridimensional space are really to differ from their own mirror images. We saw that in this respect it makes no difference whether the constituent parts of a configuration are all different from one another, or whether they are identical; because in the latter case there can be present a more or less regular symmetrical spatial distribution of such identical parts that may yet very well be different from its mirror image, if only its symmetry be purely axial. A special kind of tridimensional configuration, of particular interest to chemists, includes those atomic complexes commonly called chemical molecules.

The idea that, in order to understand the properties of chemical molecules, one must take into consideration the tridimensional architecture of such atomic complexes, is not a very old one. On the contrary it is but eighty years since Pasteur, at the outset of his brilliant scientific career, discovered those fundamental facts which constitute the very foundation of modern stereochemistry. It was during his investigations on racemic and tartaric acids in 1848 that Pasteur discovered the special isomerism of organic molecules, that taught the existence of atomic arrangements related to each other in the manner of non-superposable mirror images. Pasteur himself at once realized that this discovery makes it absolutely necessary to consider the tridimensional arrangement of the atoms within the composite molecule—whether they are disposed along right- or left-handed helices like the steps in flights of right- or left-handed winding stairs, or in some other enantiomorphic configuration. Pasteur pointed out that such enantiomorphic atomic configurations must show a

similar mechanical stability and therefore have an equal chance of being generated. They must also possess the same scalar properties: density, characteristic temperature, refraction, dispersion, solubility and the like. But they must also differ in all such physical properties as are defined by directional (vectorial) data; for example, to rotate in one direction or the other the plane of polarization of a beam of polarized light; in the unsymmetrical disposition of certain faces of their crystal forms; in the enantiomorphous distribution of pyro- and piezo-electrical polarity.

These facts are summed up in the so-called Pasteur's Law and constitute the true basis of all later stereochemical views; it is therefore desirable once again to review briefly the mode of their discovery and their scope.

In 1815 the French physicist Biot discovered that the plane of polarization of a linear-polarized beam of light will be turned through a certain angle when passing through certain crystals (quartz) parallel with their principal axes, or if it traverses the solution of any one of several naturally occurring organic substances (camphor, saccharose). Biot at once suggested that this remarkable property, this "optical activity", must be connected in some way with the special nature of the molecules of these organic substances present in their solutions. He was able also to show that in the case of quartz crystals some turned the plane of polarization to the right, others to the left. The French crystallographer Haüy formerly had stated that there are two kinds of quartz crystals, some of which had certain limiting faces in exactly inverse arrangement to the other faces, as compared with quartz crystals of another kind. In 1820 John Herschell expressed the opinion that there might be a causal connection between these phenomena, of such a character that quartz crystals having the one kind of face-distribution would also cause a deviation of the plane of polarization opposite to that observed in crystals showing the enantiomorphous arrangement of limiting faces. These facts made a deep impression on Pasteur and he was so strongly convinced of the truth of Herschell's idea that he immediately suspected the logical inconsistency of an observation by Mitscherlich. In 1844

the latter had stated that the crystal form of the strongly *dextro*-rotary sodium ammonium tartrate would be the same as that of the corresponding salt of the isomeric but optically inactive racemic acid. After accurate crystallographic comparison of a number of salts of tartaric and of racemic acids, Pasteur was soon able to state that the salts of *dextro*-rotary tartaric acid all showed an analogous and non-superposable hemihedrism—as postulated by Herschell's view—while those of racemic acid did not show any trace of it, their crystal forms being in general quite different from those of the tartrates. There was a single apparent exception, however, precisely that one indicated by Mitscherlich, the sodium ammonium racemate; but Pasteur soon found that, on recrystallizing this salt from aqueous solutions at relatively low temperatures, the product contained two different kinds of crystals. Both kinds showed similar hemihedral faces, but these were arranged in exactly opposite manner. What emotions must have seized upon the young investigator when, after carefully selecting crystals of both types, he discovered that those of the one kind gave aqueous solutions that turned the plane of polarization of the traversing light beam in a direction precisely opposite to that produced by solutions of the crystals of the other kind! Immediately he gave the only correct explanation of the fact: when recrystallizing the isomeric optically-inactive sodium ammonium racemate, the salt must have been separated into the salts of two different tartaric acids which evidently rotated the plane of polarization of the light beam in opposite directions. On deriving these acids from the *dextro-* and *levo*-rotary salts he obtained them in a pure state and proved the identity of the product with racemic acid itself by recrystallizing a mixture of equal weights of both acids.

The history of science has rarely witnessed a discovery that has so deeply influenced the thought and theoretical views both of physicists and chemists as this one by Pasteur. From the beginning he, himself, realized its overwhelming importance for the concepts of the atomic structure of the chemical molecule. No doubt whatever

could now remain that the molecules of both tartaric acids were the same in composition and structure, differing in spatial arrangement only in so far that one was the enantiomorph of the other. This could be the case, however, only if the configuration were tridimensional, and Pasteur's remarkable acuteness at once showed him that it must be the special geometrical properties of the molecules as wholes that were here the determining factors. He emphasized the fact that the one configuration was the non-superposable mirror image of the other owing to the absence of some symmetry properties in their arrangements, or as he expressed it, the existence there of a certain "dissymmetry". This view we now know to be altogether the correct one and of general application; indeed it is much more universal than were the later views of LeBel and van't Hoff. Whenever the configuration of the atoms in a molecule is such that the whole possesses symmetry which makes that configuration different from its mirror image, there is a possible isomerism in which both isomers bear the relation to each other of right-handed to left-handed figures. In the solid state they will show enantiomorphic crystals, and in solution opposite optical activity. According to Pasteur it is, therefore, not at all the completely asymmetric molecules alone that will show this isomerism. Pasteur's acute judgment in this connection has been confirmed subsequently in a very convincing way.

The great Frenchman himself, however, was not yet able to point out more precisely the spatial arrangement of the atoms in the molecules. Other suggestions were yet to be made before it would seem possible to return to his views. These suggestions came in 1874 from LeBel and van't Hoff as their idea of the tetrahedral configurations of substances of the type CX_4; and also by introducing the doctrine of the so-called "asymmetric carbon atom" into organic chemistry.

The former idea simply suggests that if a tetravalent carbon atom be linked with four like substituents X—*e.g.* four hydrogen atoms as in CH_4—the four substituents will be arranged in such a way that their mean position coin-

cides with the apices of a regular tetrahedron, the carbon atom itself occupying the geometrical center of the figure (Figure 11a).[1]

It is at once evident that this fact is a simple expression for the equal partition of space about the central atom by the four identical substituents. It is simply an illustration of the symmetrical spacing about the central multivalent atom, recently demonstrated experimentally by the Roentgen-spectroscopical work of Bragg and others on the atomic structure of the diamond. The significance of this fundamental idea of LeBel and van't Hoff is that it immediately made necessary the extension of the usual structural formulas of organic chemistry into tridimensional space; therefore it became the very starting point of all later stereochemical reasoning.

Up to the present no well-established facts can cause us to doubt this statement. Recently the case of pentaerythritol, $C(CH_2OH)_4$, and some of its derivatives, which seemed to indicate the possibility of a "pyramidal" structure, has been definitely proved to be quite in accord with the above concept,[2] its configuration in the solid state being chiefly a tetragonal bi-sphenoid, and in solution probably that of a but slightly distorted tetrahedron. If the substituents X themselves have "spherical" symmetry, then the total symmetry of the molecules CX_4 is a rather high one: three binary axes mutually perpendicular, four polar trigonal axes, and four planes of symmetry. The presence of the latter causes the whole molecule to be identical with its

[1] There may be reasons why the symmetry of this configuration may be lower; *see* K. Yardley, *Phil. Mag.*, 6, 433 (1928). In every case, however, this symmetry will be referable to several planes and the arrangement must always be superposable on its mirror-image. We must remember, however, that this is true only for quadrivalent carbon and perhaps other elements of its group; there is no *a priori* reason for supposing the same to be true for quadrivalent sulphur, as we shall see.

[2] A. Mark and K. Weissenberg, *Z. Physik*, 12, 301 (1923); *Z. Krist.*, 65, 499 (1927); F. M. Jaeger and H. Haga, *Proc. Kon. Acad. Sci. Amsterdam*, 18, 1350 (1916); H. G. K. Westenbrink and F. A. van Melle, *Z. Krist.*, 64, 548 (1927); A. Gerstacker, H. Möller and A. Reis, *Z. Krist.*, 66, 355 (1928); J. E. Knaggs, *Mineralog. Mag.*, 20, 346 (1925); E. Giebe and A. Scheibe, *Z. Physik*, 33, 760 (1925); A. Hettich and A. Schleede, *Z. Physik*, 46, 147 (1928); H. Seifert, *Sitzb. preuss. Akad. Wiss.*, 34, 289 (1927); J. Nitta, *Bull. Chem. Soc. Japan*, 1, 62 (1926); H. Möller and A. Reis, *Z. Krist.*, 68, 385 (1928).

The symmetry of these crystals seems to be highly uncertain according to: E. Ernst, *Z. Krist.*, 68, 139 (1928); A. Schleede and E. Schneider, *Z. anorg. Chem.*, 168, 313 (1928); A. Schleede and A. Hettich, *ibid.*, 172, 121 (1928); H. Seifert, *ibid.*, 174, 318 (1928); A. Nehmitz, *Z. Krist.*, 66, 313 (1928). F. A. van Melle, Dissertation, (Groningen, 1928).

mirror image, so that isomerism of the kind here considered can never occur. Van't Hoff's well-known hypothesis concerning the "free rotation" of the substituents X round their single bonds to the central atom, introduces into his theory precisely those conditions required to give X itself the highest possible symmetry, viz., spherical. The single exception here is the special case when the substituents themselves are *dextro-* or *levo-*gyrate; such cases will be considered later on.[1]

Let us now suppose that the substituents X_4 are replaced in order by other substituents X′, X″, X‴, all different from X and from each other. What changes in the symmetry of the molecule will this cause?

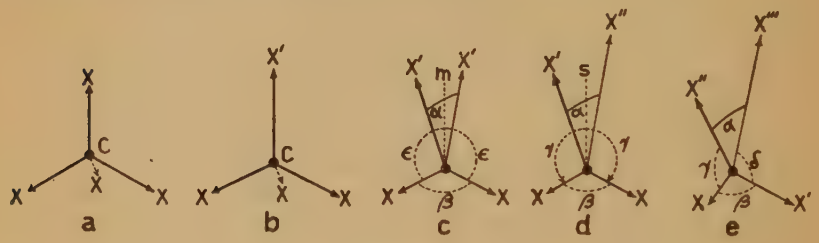


FIG. 11

In CX_4 (Figure 11a) the distances C-X are all equal because all the Xs are identical and therefore exert the same force on C or are affected by C in exactly the same way. In the molecule CX_3X' however, this is no longer true; the distances C-X now differ from C-X in CX_4 while remaining equal to one another, but C-X′ is certainly larger or smaller than the others.

The complex CX_3X' (Figure 11b) therefore certainly has a symmetry different from that of CX_4. At the most it can have a polar ternary axis parallel to C-X′, and three planes of symmetry passing through it; but the presence of these planes of symmetry again makes the molecule identical with its mirror image, notwithstanding all changes, so that no isomerism in the sense of Pasteur is possible here.

[1] F. M. Jaeger, *Lectures on the Principle of Symmetry* etc., page 239, 259 (2d ed., Amsterdam, 1920).

If a second X is replaced by X′ we have the configuration shown in Figure 11c. Here the molecule possesses a single polar binary axis bisecting the angle α between the C-X′ directions and the angle β between two C-X directions. It also has two planes of symmetry mutually perpendicular and passing through the binary axis. In this case also no isomerism can occur. If, however, two Xs are replaced by X′X″ the configuration will be that shown in Figure 11d, and now the molecule can possess at most a single plane of symmetry passing through X′X″ and the central carbon atom; but even here the presence of a plane of symmetry prohibits the appearance of an enantiomorphic configuration. The same is true for a derivative having the formula CC′X′X″$_2$, where the only plane of symmetry still present now passes through XX′ and the central carbon atom.

When we pass to the formula CXX′X″X‴, the situation is totally changed. Now C-X, C-X′, C-X″ and C-X‴ are all different and the original tetrahedron of CX_4 has changed to an irregular tetrahedral arrangement that is wholly asymmetrical (Figure 11e). Now there are two such irregular tetrahedrons having a right- and left-hand relationship, being enantiomorphous and not superposable except through mirror reflection. Therefore the compound CXX′X″X‴ must exist in two isomeric forms, one being the non-superposable mirror image of the other.[1]

The LeBel-van't Hoff theory recognized this case as that of the "asymmetric carbon atom." Its true meaning is that if the central carbon atom be linked to four different substituents, the spatial division above ceases to be symmetrical and therefore this spatial distribution may be effected in two different ways, the one being enantiomorphous to the other. The LeBel-van't Hoff thesis is that, if a molecule contains a carbon atom linked in this manner to four different substituents, the molecule as a whole certainly will also lack any symmetry elements in its space division; therefore it must exist in two enantiomorphous

[1] One still frequently meets the original representation of this case as a regular tetrahedron with four unequally occupied quarters, a wrong and misleading presentation. The regular tetrahedral arrangement CX_4 could not possibly be preserved if X, X′, X″ and X‴ are different.

configurations corresponding to what Pasteur would have called two isomerides. We shall see, however, that this is true only if the molecules contain but a single asymmetric carbon atom; if several of these are present, it is quite possible that the molecule as a whole is no longer asymmetric.

The theory of the asymmetric carbon atom has proved to be wonderfully far reaching; even today it is one of the most frequently employed heuristic principles used by the chemist in deciding whether he may be able to separate an optically inactive substance into its optically active antipodes. It holds true not only in the case of tetravalent carbon, but for other multivalent atoms whose valency exceeds three, for instance: tetravalent sulphur,[1] selenium,[2] tin,[3] silicon,[4] boron,[5] pentavalent nitrogen,[6] arsenic,[7] phosphorus.[8]

It must be emphasized again in this place, that in all these cases the specific nature of the multivalent atom must be considered as determining the symmetry of the spatial distribution about it. In the first place it is not at all necessary that the mode of orientation of the four "valencies" of quadrivalent Se or S—atoms that are usually bivalent in contrast to C, Si, etc.—be the same as that for the carbon atom. In fact later we shall meet phenomena of tetravalent sulphur which clearly indicate that it is not permissible to extend conceptions deduced from the behavior of the carbon atom in this respect to other elements like S, Se, and N.

The whole concept of asymmetric atoms must be considered as an incomplete and rudimentary one. The funda-

[1] W. J. Pope and S. J. Peachy, *J. Chem. Soc.*, 77, 1072 (1902); S. Smiles, *ibid.*, 77, 1174 (1900).

[2] W. J. Pope and A. Neville, *J. Chem. Soc.*, 81, 107, 1552 (1902).

[3] W. J. Pope and S. J. Peachy, *Proc. Chem. Soc.*, 16, 42, 116 (1900); A. Werner, *Lehrbuch der Stereochemie*, p. 316 (Jena, 1904).

[4] F. S. Kipping, *J. Chem. Soc.*, 91, 209, 717 (1907); 93, 457 (1908); 95, 69, 408 (1909).

[5] J. J. Boëseken and J. Meulenhoff, *Proc. Acad. Sci. Amsterdam*, 27, 174 (1924).

[6] F. S. Kipping, *J. Chem. Soc.*, 83, 873, 918 (1903); W. J. Pope and S. J. Peachy, *J. Chem. Soc.*, 75, 1127 (1899); W. J. Pope and Hearvey, *ibid.*, 79, 829 (1901); J. Meisenheimer and collab., *Ber.*, 41, 3966 (1908); *Ann.*, 428, 252, 254, 269, 278 (1922); E. Wedekind, *Z. Physik. Chem.*, 45, 235 (1903); *Zur Stereochemie des Fünfwertigen Stickstoffs*, (Stuttgart, 1909).

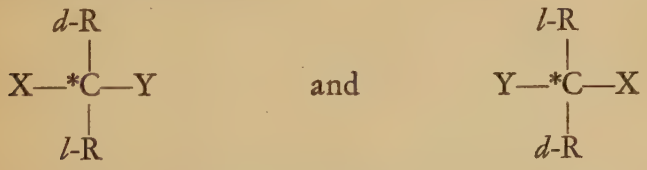
[7] T. F. Winmill, *J. Chem. Soc.*, 101, 718 (1909); *Proc. Chem. Soc.*, 28, 93 (1912). Optically active compounds are probable, but have not yet been obtained in this case.

[8] J. Meisenheimer and L. Lichtenstadt, *Ber.*, 44, 356 (1911); F. S. Kipping, *J. Chem. Soc.*, 99, 626 (1911).

mental truth of the general principle underlying the phenomena of optical isomerism, has been disturbed by bringing to the fore a mere special case of a more general principle, as if it were the fundamental and exhaustive one.

The doctrine of the asymmetric carbon atom considers two different factors simultaneously. They are mutually superposed, but need not necessarily be mutually connected. The whole conception lies in the idea of the "chemical contrast" between the substituents as well as their dissymmetric spatial arrangement. This last factor is by no means necessarily connected with a difference between the separate parts (patterns) of such arrangements, as we saw in the first lecture.

There is yet another difficulty attaching to the doctrine of the asymmetric carbon atom and its application as a criterion of the possible resolvability of the molecules in which it is present. How shall we define it in a final and universally valid manner? So far this question has remained unanswered.[1] As the result of many discussions and arguments between scientists the best possible definition is the following: An asymmetric carbon atom is one having its four valencies linked to four substituents each different from the other in both composition and structure. Even this definition, however, does not hold. Consider, for example, the following molecules:



in which R is an unsymmetrically constructed radical such as $CHCl(SO_3H)$, the arrangements of its substituents being

clockwise in *d*-R and counter-clockwise in *l*-R. Now since *d*-R and *l*-R have identical compositions but different structures, the central C atom is, according to definition,

[1] It is only when the electronic conception of chemical linkage is considered, that the following definition can be given: An asymmetric carbon atom is one in which the linking electrons are unsymmetrically distributed in space about it.

undoubtedly an "asymmetric" carbon atom designated by the *C. However, in spite of its presence in these two molecules, they cannot exist in enantiomorphous forms because they possess a plane of symmetry passing through X—*C—Y, and they are, therefore, identical with their mirror images.[1]

On the other hand, in the molecules:

there is no "asymmetric" carbon atom present, according to the definition. Nevertheless, these two molecules are completely unsymmetrical and therefore may exist in two enantiomorphous forms.[2]

These considerations also illustrate the inadequacy of the whole theory. Here again only a consideration of the particular symmetry of the molecule as a whole can guard us against drawing erroneous conclusions and indicate with certainty whether the molecule can be successfully resolved into its possible antipodes.

We have emphasized the fact, that geometrical complexes and spatial arrangements may very well consist of identical structural units, while yet appearing in enantiomorphously related forms, provided the arrangement of those identical units is such that the whole configuration possess merely axial symmetry. Pasteur's postulated "dissymmetry," including the possible occurrence of right and left-hand isomerides, is, therefore, by no means exclusively dependent, for its occurrence, on a chemical difference between the constituent unities of the complex under consideration. Even if they are identical it is possible for the molecule as a whole to show such a non-superposable symmetry of its configuration. This will be illustrated more fully in the next chapter.

[1] For example, ribotrihydroxyglutaric acid does not exist in two optically active forms.

[2] This is why arabotrihydroxyglutaric acid is known both in a *dextro-* and in a *levo*-rotary form.

CHAPTER III

Molecules Showing Non-superposable Symmetry

In order to explain and illustrate the relations that obtain where the molecule as a whole shows a non-superposable symmetry of its configuration, I select first a very pronounced and convincing example. We know a whole series of salts, derived from so-called "complex ions," which contain three molecules of a bivalent pseudo-base or three ions of a bivalent acid, in addition to a trivalent central metal atom. We shall here consider in particular, those cases where the metal atom is cobalt, rhodium or the like, and the pseudo-base is ethylenediamine,[1] NH_2-CH_2-CH_2-NH_2. A number of facts compel us to assume that there are six positions in space, distributed as the corners of an octahedron having the metal atom in the center, while each of the six corner positions is occupied by one amino group of the base and held there in some way by binding forces. The ethylenediamine molecule is highly symmetrical: it possesses at least a binary axis,[2] and in the liquid state probably a pair of symmetry planes also.

Figure 12 will give you an idea of the special manner in which the three ethylenediamine molecules are distributed in space about the central metal atom. The whole configuration is a highly symmetrical one: it is evident that the resulting complex ion has a trigonal axis and three polar binary axes lying in a plane perpendicular to the trigonal axis; but there are neither symmetry planes nor a symmetry center. The whole ion therefore has merely axial symmetry of the same kind as that possessed by quartz crystals. Just as right-handed and left-handed quartz crystals occur in nature, so these ions are found to occur in two enantiomorphous configurations. Actual

[1] [The editors have endeavored to make the terminology of this volume conform to the best American usage. Special thanks are due Professor John R. Johnson for supervising this feature of the work.—Ed.]

[2] W. G. Burgers, Dissertation, p. 118. (Groningen, 1928).

experience has taught us that there are two series of salts, related to each other as right- and left-hand isomerides, whose solutions exhibit strong and oppositely directed optical activity. Their crystal forms also appear to be each other's mirror images. In fact this is a perfect case of Pasteur's isomerism.

In this case, however, there is no chemical contrast whatsoever between the three substituents about the central metal carbon atom. All the substituents are quite identical, and the only cause of the isomerism and of the optical activity—here incomparably greater than is ever met with

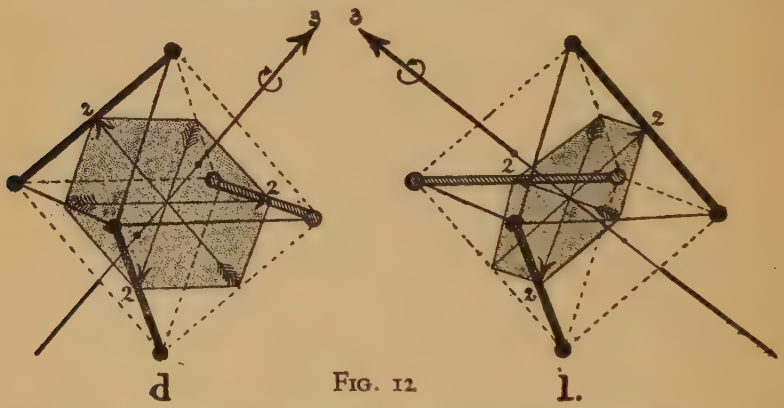
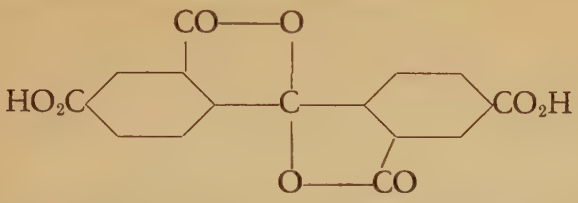


FIG. 12

in carbon compounds—is the dissymmetrical spatial disposition of these identical substituents, as supposed by Pasteur. We have here no "asymmetrical atom" in the sense of the LeBel-van't Hoff theory; on the contrary the division of space about the central atom is a pronouncedly symmetrical one and precisely the same as that in the quartz crystals, which no one ever doubts to be symmetrical objects.

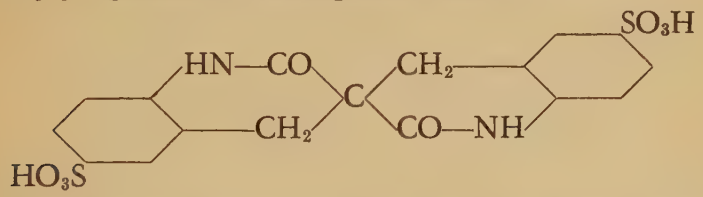
It seems desirable to give further illustrations of the fact that the LeBel-van't Hoff concept, that an "asymmetric atom" must be present in the molecule as a condition for the possible occurrence of enantiomorphously related isomers, is not sufficiently general in its scope. This special isomerism may be present even in carbon compounds, when there is no asymmetric carbon atom present

in the molecule. For example, the keto-dilactone of benzophenone-2,4,2′,4′-tetracarboxylic acid:



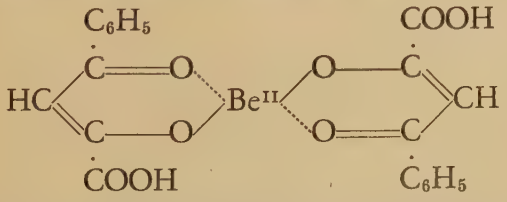
has been resolved into its optically active antipodes.[1] The reason for this is that, taking the tetrahedral configuration about each carbon atom into account, the whole molecule appears to possess only a single binary symmetry axis passing through the central carbon atom. The molecule, therefore, has merely axial symmetry and so differs from its mirror image.

A quite analogous case is that of bisdihydrocarbostyril-3,3′-spirane-6,6′-disulphonic acid:



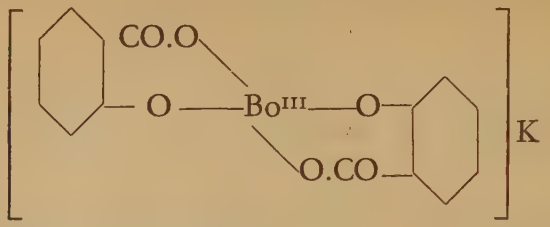
This, also, could be resolved[2] into its right- and left-hand configurations, whose specific optical rotations appear to be very large indeed. Here again no asymmetric carbon atom is present, in the sense of LeBel-van't Hoff, but only a binary axis passing through the central carbon atom.

The same phenomenon has been observed recently[3] in the case of the complex beryllium salt of benzoylpyruvic acid, probably having the constitution:



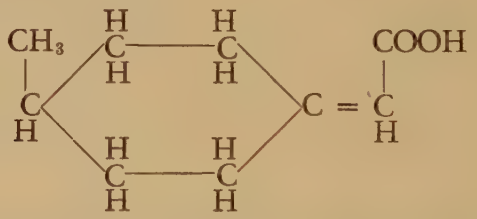
[1] W. H. Mills and C. R. Nodder, *J. Chem. Soc.*, **117**, 1407 (1920).
[2] H. Leuchs, E. Conrad and H. von Katinsky, *Ber.*, **55**, 2131 (1922).
[3] W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, **129**, 3121 (1926).

A similar case is that of potassium disalicylato-borate:



which has been resolved by means of its strychnine salt, into its optical antipodes.[1] I shall take up these cases in more detail later on.

One of the first examples of the resolvability of carbon compounds into their optical antipodes when the classic asymmetric carbon atom is absent, was studied by Pope, Perkin and Wallach.[2] The subject was 1-methylcyclohexylidene-4-acetic acid:



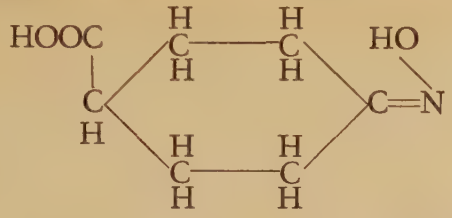
This molecule has no symmetry at all; its complete asymmetry involves the possibility of two isomerides, but is not due to any asymmetric carbon atom. Van't Hoff himself had formerly suggested that a similar case, compounds of the type

must be resolvable into optically active antipodes, because of the complete asymmetry of the molecule. Such compounds have not yet been studied from this point of view.

[1] J. Boërseken and I. Meulenhoff, *Verslag Akad. Wetenschappen Amsterdam*, 33, 22 (1924).

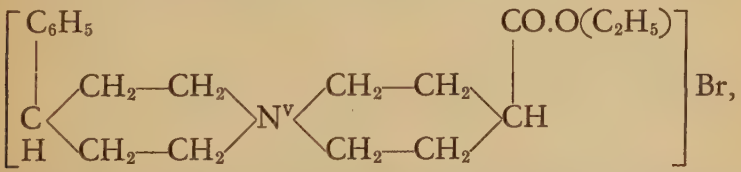
[2] W. J. Pope, W. H. Perkin, Jr., and O. Wallach, *J. Chem. Soc.*, 95, 1789 (1909); W. J. Pope and W. H. Perkin, Jr., *J. Chem. Soc.*, 99, 1510 (1911); P. F. Frankland, *ibid.*, 1 1, 654 (1912).

A similar case[1] is that of the oxime of cyclohexanone-4-carboxylic acid:

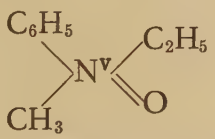


This molecule appears to have only a plane of symmetry perpendicular to the plane of the ring; but evidently the HO group is situated outside this apparent symmetry plane—in accordance with Werner's and Hantzsch's view that in the oximes the three valencies of the nitrogen atom are not situated in the same plane—therefore this is not a true plane of symmetry. The molecule therefore is completely asymmetric without possessing an asymmetric carbon atom.

In this connection we may also mention some derivatives of pentavalent nitrogen having the type of the ammonium salts. For example, 4-phenyl-4′-carbethoxybis-piperidinium-1,1′-spirane bromide:



which was resolved into its optical antipodes by Mills and Warren,[2] thus clearly demonstrating the tetrahedral arrangement of the linkages about the pentavalent nitrogen atom. That they are not arranged in a plane is proved also by Meisenheimer's resolution of methylethylaniline oxide:[3]

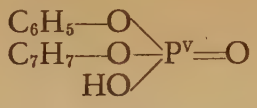


[1] W. H. Mills and A. M. Bain, *J. Chem. Soc.*, **97**, 1866 (1910).

[2] W. H. Mills and Warren, *J. Chem. Soc.*, **127**, 2507 (1925).

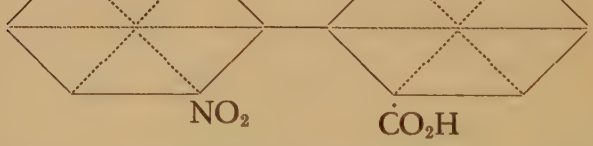
[3] J. Meisenheimer, *Ber.*, **41**, 3966 (1908); T. M. Lowry, *Phil. Mag.*, **45**, 1105 (1923). The corresponding ethyl derivative was separated by Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 2356 (1911).

If phenyl-*p*-tolylphosphoric acid:



is converted into the *l*-menthylamide, fractional crystallization will separate it into two optically active isomerides;[1] and the same is true for phenyl-*β*-naphthylphosphoric acid.[2] Here it is the arrangement of the radicals about the pentavalent phosphorus atom, that causes the dissymmetrical structure and the resolvability into optical antipodes.

The need for an early extensive survey of all cases of such resolvability of organic compounds that lack asymmetrical carbon atoms and have only axial symmetry, is emphasized by one of the most unexpected instances of this kind, viz. *γ*-dinitrodiphenic acid and some of its derivatives. This compound, studied by Christie and Kenner,[3] has the formula:



and therefore apparently a symmetry center. But if the two rings of this aromatic compound do not lie in the same plane, the symmetry center disappears and is replaced by a single polar binary axis as shown in Figure 13. I think this is the best way to explain the phenomena of optical isomerism here observed.[4] The molecule now possesses only axial symmetry and must therefore be re-

[1] B. D. W. Luff and S. Kipping, *J. Chem. Soc.*, **95**, 1993 (1905).
[2] S. Kipping and F. Challenger, *J. Chem. Soc.*, **99**, 1626 (1911).
[3] J. Kenner and C. H. Christie, *J. Chem. Soc.*, **121**, 614 (1922); **123**, 779 (1923).
[4] The British authors themselves give another formula to explain these facts, which is based on former views set forth by Kaufler. Their formula supposes the ring planes to be parallel and the authors find here *cis* and *trans* forms, the latter being the resolvable one. However the fact is explained equally well by turning the coaxial planes through less than 90°.

solvable into optical antipodes as experiment has proved. The same is true in the case of the tetranitro-derivative of

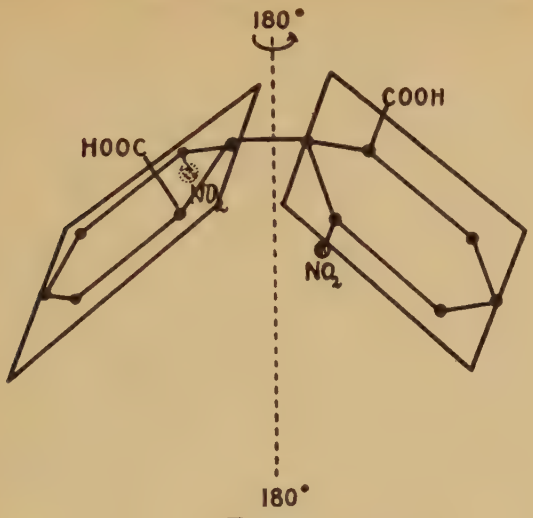
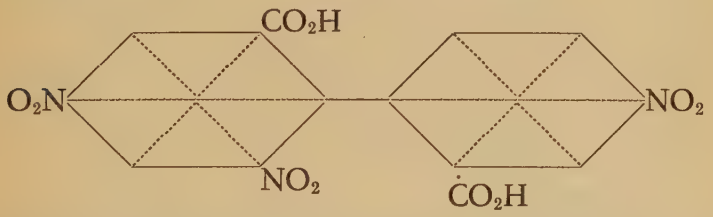
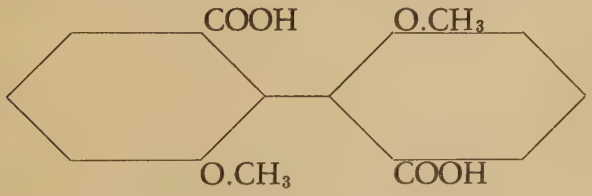


FIG. 13

this acid, as well as the trinitro-derivative which is 4,6,4′-trinitrodiphenic acid, and has the formula:



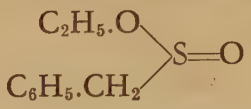
This could be split into optically active antipodes. In this case the molecule has no symmetry at all and the optical rotations are relatively strong. Recently Kenner and Turner[1] succeeded in resolving 6,6′-dimethoxydiphenic acid:



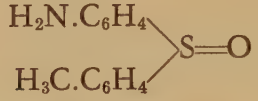
[1] J. Kenner and H. A. Turner, *J. Chem. Soc.*, 2340 (1928).

into its optical antipodes with the aid of its quinine salt, and found its specific rotation $[\alpha]_D$ to be $-115°$.

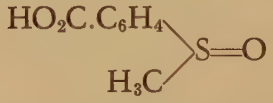
Other cases are ethyl-*p*-toluenesulphinate:

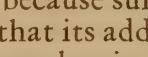


studied by Phillips;[1] 4′-amino-4-methyldiphenyl sulphoxide:



and *m*-carboxyphenylmethyl sulphoxide:

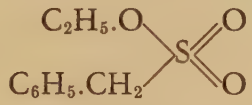


both of which were investigated by Harrison, Kenyon and Phillips.[2] Here on oxidation of the S=O group to an SO_2 group, the optical activity is lost so that the cause of the asymmetry must be the fact that both of the carbon-containing substituents are always located outside the plane of the S=O group, or at least the plane containing the groups C_2H_5O and $C_6H_5.CH_2$, as in the first compound, cannot be perpendicular to that containing the S=O group. An analogy with corresponding carbon compounds, *e.g.* the ketones of the formula  , may not be stressed in this respect because sulphur is usually bivalent and we may not assume that its additional valencies will behave exactly like the four valencies of the carbon atom.

In this connection I would draw attention to the fact that carbon, as diamond, crystallizes in the cubic system, the carbon atoms being so arranged in space that the tetrahedral configuration of their valencies is preserved. On the other hand, sulphur crystallizes in the rhombic system and it is well known that in the rhombic bisphenoid

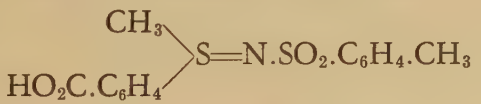
[1] H. Phillips, *J. Chem. Soc.*, 127, 2552 (1925).
[2] Harrison, Kenyon and Phillips, *ibidem*, 128, 1079 (1926).

for instance, the lines joining its corners with the center lie in two planes at an oblique angle with each other. If the plane containing the radicals $C_2H_5.O$ and $C_6H_5.CH_2$ makes an oblique angle, say 45°, with that containing the group S=O, the molecule is completely assymetric and therefore must occur in two enantiomorphous configurations. This view also furnishes a ready explanation of the fact that the two bonds of the S=O group do not have like properties. If the compound is oxidized to the sulphone,



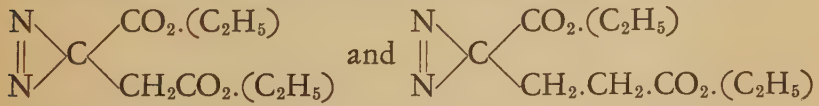
then it is highly probable that the two double-linked O atoms lie in two mutually perpendicular planes, and now the plane of the C_2H_5O and $C_6H_5.CH_2$ groups bisects the angle between the two planes first mentioned. The molecule now will have a symmetry plane and the optical activity is lost. This has been actually observed.

A similar case—analogous to that of a pyridylhydrazone considered on page 59—is that of *m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine:



which was separated into its antipodes by Clarke, Kenyon and Phillips[1] with the aid of cinchonidine. In contrast with the other cases described, where the racemic and optically active compounds were very similar to one another, in this case the antipodes and the racemic substance had very different properties.

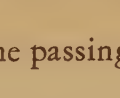
Perhaps we may also mention in this connection the optically active diazosuccinic and diazoglutaric esters:



investigated by Noyes and Chiles,[2] neither of which pos-

[1] S. G. Clarke, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 188 (1927).

[2] W. A. Noyes and H. M. Chiles, *J. Am. Chem. Soc.*, 44, 1798 (1922); W. A. Noyes and C. Marvel, *ibidem*, 42, 2259 (1921).

sesses an asymmetric carbon atom in the proper sense of the word. In this case, also, the molecule can be unsymmetrical only if the plane passing through  makes an oblique angle with that passing through .

These illustrations will suffice to demonstrate to you the inadequacy of the theory of the asymmetric carbon atom to serve as a criterion for the possible resolvability of inactive compounds into their optically active antipodes. The case brought forward by LeBel and van't Hoff is only a very special case covered by Pasteur's much broader principle. It applies only to the case in which, by reason of a wholly asymmetrical space-division about one of the carbon atoms, the molecule lacks all symmetry. Pasteur's conception, however, embraces all cases, including those where the molecule does not contain such asymmetric atoms but may eventually be built up by identical substituents distributed dissymmetrically in space. His notion of "dissymmetry" signifies the lack of symmetry properties of the second order; or in modern language: the existence of axial symmetry only in the molecule as a whole.

If the tetrahedral configuration of methane and the like is accepted as proposed by LeBel and van't Hoff; if moreover the experimental facts be taken into account, that evidently three valencies of the carbon atom are never situated in the same plane; and if the view be adopted that the substituents and radicals—with the exception of the only case that they themselves show a completely asymmetrical space distribution—may be considered as possessing the highest possible (spherical) symmetry;[1] then the

[1] It must be remembered that this position is wholly determined by van't Hoff's view of the free rotation of such radicals about the line joining them with the central carbon atom, if the link between them is a simple one and the molecules are freely moving in a liquid or a gas. For the crystalline state, for instance, it is no longer valid, as the atoms of a crystalline structure are in nearly fixed positions; in such cases it is therefore necessary to take the special proper symmetry of such radicals, CH_3, NH_2, NO_2, into account.—*See* K. Weissenberg, *Z. Elektrochem.*, **32**, 470 (1926).

best way for judging whether the molecule considered might be resolved into their antipodes or not, is to construct their stereometric models and to study the symmetry of the whole. If the model is asymmetrical or possesses only axial symmetry for the whole, then it is certain that there is good prospect of success with experiments aiming to resolve them into optical antipodes. Of course, as we have seen in the cases of γ-dinitrodiphenic acid and the oxime of cyclohexanone-4-carboxylic acid, there may be special circumstances of mutual attraction between the different parts of the molecule, distorting the configuration in an unexpected way and making them of lower symmetry than the apparent one. Rare as they are, such cases have particular interest for the chemist.

Thus it is only experiment in each case that will teach us whether the symmetry of the molecule really permits nonsuperposable mirror images. It is one of the chief problems in the organic chemistry of the future to discover such new cases of optical isomerism when there are no asymmetric atoms present in the molecule.

The question may arise: would it not be preferable to completely abandon the doctrine of the asymmetric atoms? From the theoretical point of view the asymmetric carbon atom is a superfluous conception; it may be preserved, however, as a guide to the practical chemist in deciding whether or no he shall look for optical isomerides. The doctrine of the asymmetric atom has done splendid service in stimulating innumerable experimental investigations, and in this capacity has been a necessary link in developing our stereochemical views. After coming so far, however, and standing now on the shoulders of the earlier workers, we must have a broader outlook than our predecessors. We must now acknowledge that the conception of the asymmetric atom embraces only a special, and not even a simple, case of the much more general view, namely, the symmetry relations of the molecule in its totallity; and we should not stick too persistently to the more restricted and often rather vague notion of "asymmetric" atoms. It is increasingly necessary—especially with the experience gathered during the last ten years—

to realize that the doctrine of the asymmetric atom should no longer be regarded as a fundamental concept in our views of the connection between molecular composition and the optical activity of solutions. Evidently the fundamental and determining factor is always the spatial distribution of a number of linking electrons about the plurivalent atoms; and this distribution determines, primarily, the magnitude of the qualitative and quantitative effect. In most cases the positions of the linking electrons have been indeterminable until now; therefore we usually are seeking the material supporters, the atoms and radicals. Since these electrons are intimately connected with the constituent atoms and substituents by attracting forces within the molecule considered, there appears to be a close parallelism between atomic configuration and the optical activity of the molecule. But this connection is only a secondary one; so that in general it will be impossible to determine a rigorous relationship between the magnitude of the optical rotation shown by the molecule and the material nature of the substituents surrounding the central carbon atom. It is for just this reason that it is not sound principle to introduce into our science an argument based on the chemical contrast between the possible substituents, as is done by the LeBel-van't Hoff theory. As we shall see in the case of the complex cobalt and rhodium salts with ethylenediamine, the chemical contrast between the substituents has no appreciable influence on the absolute magnitude of the specific optical rotary power of the molecule. This power seems to be due in large part, if not exclusively, to the paticular tridimensional arrangement of the substituents—or rather of their linking electrons. These influences also determine its dependency on wavelength, *i.e.* its rotatory dispersion. All other influences are but secondary phenomena.

CHAPTER IV

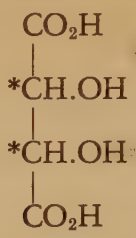
Symmetry and Resolvability of Organic Molecules; Study of Complex Salts

In the last chapter I tried to give you an idea of the way in which the principle of symmetry can be applied to problems dealing with the possibility of separating an optically inactive substance into its enantiomorphous antipodes. I emphasized the historical rôle of the LeBel-van't Hoff theory in developing our modern stereochemical views and its position as a special case of the more universally valid conceptions concerning the symmetry of tridimensional structural formulas. The theory was a necessary step in the whole development of our ideas concerning atomic arrangements in space. In particular the concept of the tetrahedral space-division about the tetravalent carbon atom appears to be a result of permanent value.

I have remarked already that, in the case of molecules containing more than one single asymmetrical carbon atom, there is no simple answer to the question as to whether the molecule under consideration is resolvable or not. In these more complicated cases, however, it would seem that the study of the symmetry of models constructed on the supposition of tetrahedral configuration of the groups about each carbon atom, might give us sufficient information as to the possibility of the resolution into optically active isomerides. The following examples will illustrate this idea in detail.

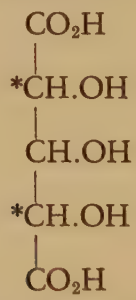
One of the oldest known instances of a compound having two asymmetric carbon atoms in its molecule is meso-

tartaric acid, whose formula is usually written thus:



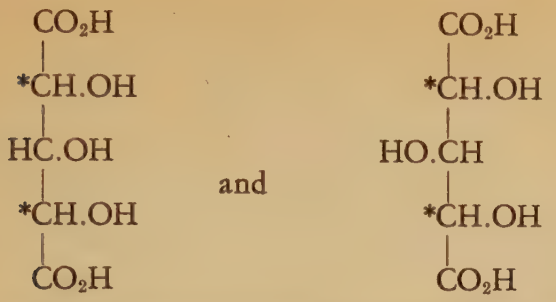
where the asymmetric carbon atoms, according to the LeBel-van't Hoff theory, have asterisks. The arrangement of the four groups or substituents about each of them is enantiomorphic for both carbon atoms. The whole molecule therefore possesses a center of symmetry situated midway between the two asymmetric carbon atoms. As these are symmetry elements of the second order, no resolution into optical antipodes is possible here and this, indeed, is what experiment has taught us.

An analogous, though somewhat different, case is presented by trihydroxyglutaric acid:



Here, as in the preceding case, the arrangement about the two asymmetric carbon atoms is enantiomorphous. The carbon atom in the middle of the chain is, by definition, asymmetric. But this molecule, ribotrihydroxyglutaric acid, is non-resolvable for the same reason as that given for mesotartaric acid, the plane through the central CH.OH group being a symmetry plane.

If, however, the configuration about both asymmetric carbon atoms is identical, as in arabotrihydroxyglutaric acids, both molecules,



are each other's non-superposable mirror images and, indeed, two enantiomorphic isomers of this acid have been separated.

Another instructive example is presented by the 3,6-dimethyl-2,5-diketopiperazines, which can occur in either a *cis* or a *trans* form (Fig. 14a):

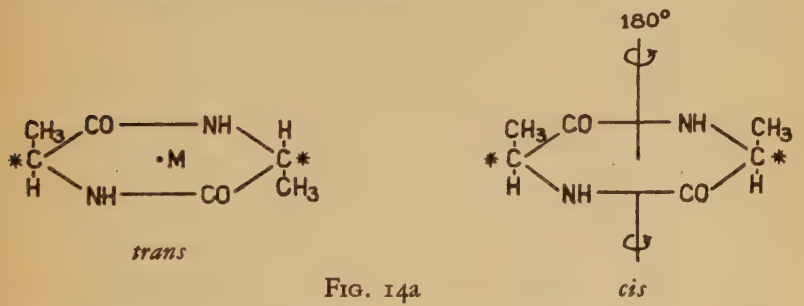


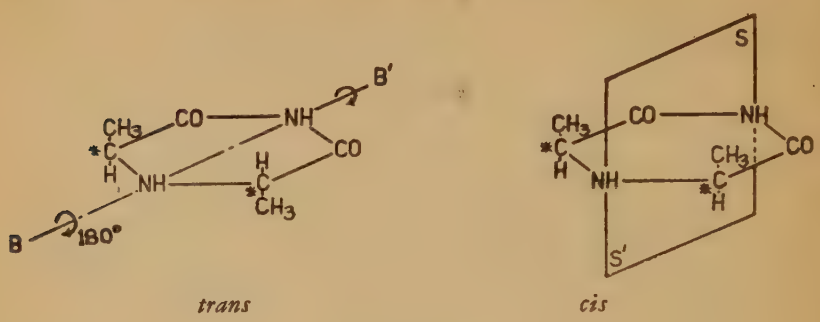
FIG. 14a

The *trans* form evidently has a center of symmetry at M—in the plane of the ring—which is a symmetry element of the second order; therefore this compound must be identical with its mirror image and cannot be resolved into optical antipodes, as Ladenburg has proved.[1] The *cis* form on the contrary evidently presents a single binary axis perpendicular to the plane of the ring; thus it has only axial symmetry and differs from its mirror image. Fischer and Raske[2] have shown that the *cis* form exists as a racemoid that can be separated into a *dextro-* and a *levo*-rotary antipode.

[1] A. Ladenburg, *Ber.*, 28, 1955, 3104 (1895); P. Groth, *ibidem*, 28, 2510 (1895).

[2] E. Fischer and K. Raske, *Ber.*, 39, 467, 3981 (1906).

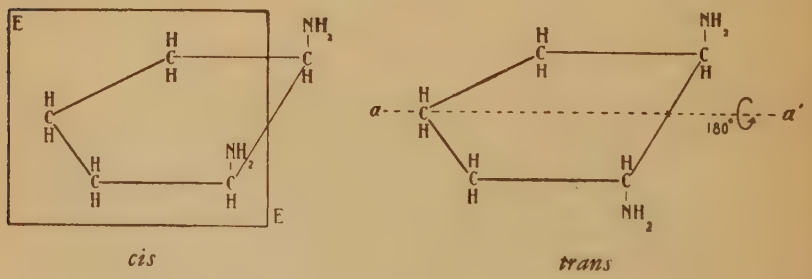
In the case of the 2,6-dimethyl-3,5-diketopiperazines which also can occur in a *cis* and a *trans* form (Fig. 14b):



trans *cis*

FIG. 14b

the *cis* form evidently has a plane of symmetry *SS'* perpendicular to the ring and is therefore unresolvable; while the *trans* form has only a binary axis *BB'* lying in the plane of the ring and is separable into two enantiomorphous isomerides. These two compounds have not yet been studied in this respect, but a similar case, that of the *cis* and *trans*-cyclopentane-1,3-dicarboxylic acids, has been



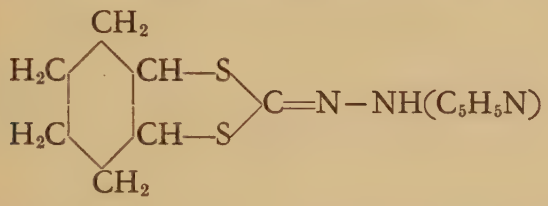
cis *trans*

FIG. 15

investigated recently.[1] The *cis* form was found to be irresolvable, while the *trans* form was obtained in *dextro* and *levo*-rotary isomerides. Such facts were also pointed out by Douris in 1919.[2] A short time ago we were able to

[1] W. H. Perkin and H. A. Scarborough, *J. Chem. Soc.*, **120**, 1400 (1921).
[2] R. Douris, *Bull. sci. pharmacol.*, Nos. 7–10, (1919).

prove the same for *trans*-1,2-cyclopentylene-1,2-diamine;[1] which has a binary axis *aa'* in the plane of the ring only, while the unknown *cis* form has a symmetry plane perpendicular to the cyclopentane ring, and therefore is irresolvable (Fig. 15). An interesting case is that of the pyridylhydrazone of cyclohexylene dithiocarbonate:[2]



which has no plane or center of symmetry and for the same reason is resolvable into enantiomorphous isomers. The optical antipodes could not be obtained in a perfectly

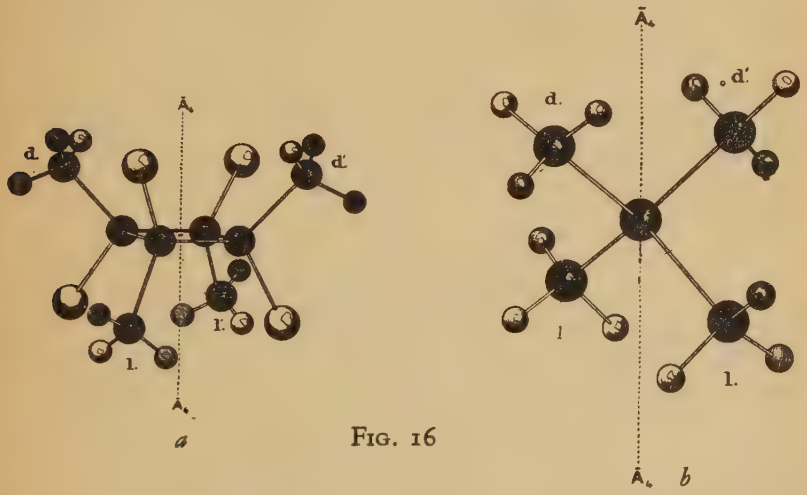


FIG. 16

pure state; but their existence has been proved beyond doubt. Here the ring has two assymetric carbon atoms, but the molecule would be inseparable into optically active isomers—just as mesotartaric acid is—were it not

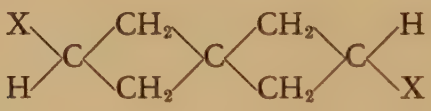
[1] F. M. Jaeger and H. B. Blumendal, *Proc. Acad. Sci. Amsterdam*, 31, 637 (1928); *Z. anorg. allgem. Chem.*, 175, 167 (1928).

[2] W. H. Mills and H. Schindler, *J. Chem. Soc.*, 123, 312 (1923).

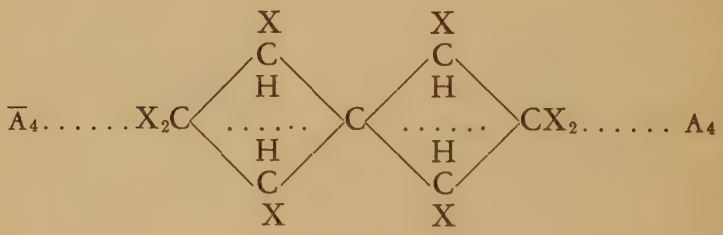
that the apparent plane of symmetry passing through $C=N-NH(C_6H_5N)$ disappears in this case for the same reason as in the oxime of cyclohexanone-4-carboxylic acid.

Molecules having four asymmetrical carbon atoms, as shown in the preceding figure (Fig. 16a and b)—in which d and d′ represent *dextro*-, l and l′ *levo*-arranged configurations of the same substituents about the carbon atoms—cannot be resolved into optical antipodes. They are identical with their mirror images because their sole symmetry element is a quaternary mirror axis $\bar{A}_4$, which we have seen to be a characteristic symmetry element of the second order.

The asymmetric molecule:



is resolvable into optically active antipodes; but the more complicated compound:

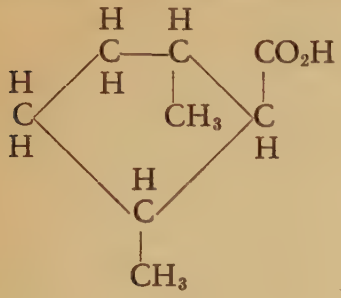


cannot be split into antipodes, because it possesses a single quaternary mirror axis $\bar{A}_4$.

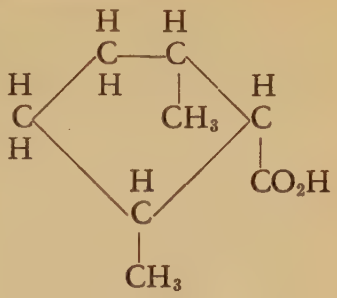
Wislecenus[1] obtained three isomeric 2,5-dimethyl-cyclopentane-1-carboxylic acids, two of them (*I* and *II*) are *cis-cis* forms and both have a single plane of symmetry perpendicular to the plane of the ring. The third (*III*) is a

[1] J. Wislecenus, *Ber.*, 34, 2572 (1901).

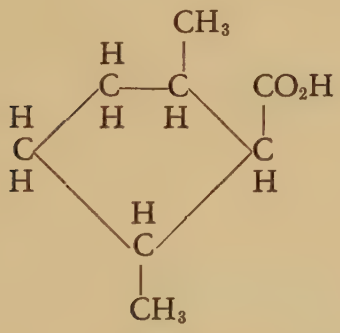
cis-trans form which has no symmetry at all; it may therefore be separable into two optical antipodes, but so far this has not been demonstrated experimentally.



I.



II.



III.

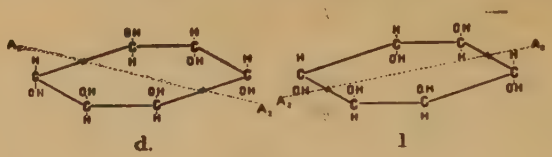
Isomeric 2,5-dimethylcyclopentane-1-carboxylic acids

In this connection the work of Von Baeyer and of Perkin[1] concerning the 1,2-, 1,3-, and 1,4-cyclohexanedicarboxylic acids is of interest. Both the *cis*- and the *trans*-1,4-cyclohexanedicarboxylic acids have a plane of symmetry and therefore are non-resolvable. The same is true for the *cis* forms of the corresponding 1,2 and 1,3 acids. But the *trans*-1,2- and *trans*-1,3-cyclohexanedicarboxylic acids have only a binary axis, and Werner and Conrad[2] succeeded in splitting the *trans*-1,2 acid into optically active components.

[1] A. von Baeyer, *Ann.*, **245**, 103 (1888); **251**, 257 (1889); **258**, 1145 (1890); W. H. Perkin, Jr., *J. Chem. Soc.*, **59**, 798 (1891).

[2] A. Werner and H. E. Conrad, *Ber.*, **32**, 3046 (1899).

A remarkable case is also furnished by the inositols, which are hexahydroxycyclohexanes. Two of them (Fig. 17)



d. l

FIG. 17

have only a single binary axis in the ring plane and thus may be separated into optical antipodes.[1] There are, however, a number of isomeric inositols: phaseomannitol, quercitol, cocositol, and the like, that evidently are non-resolvable because their configurations have planes of symmetry or a symmetry center in addition to symmetry axes.[2]

Having explained the application of symmetry principles in determining the resolvability or non-resolvability of organic molecules into optical antipodes, I now proceed to its application in studying complex salts, the special purpose of these lectures. First, however, I will interpolate some remarks on the methods of separation heretofore employed, and the difficulties encountered.

Here again we are indebted to Pasteur for the methods, although the special conditions of the experiments were not fully elucidated until physical chemistry was applied to them. In spite of the notable advances that have been made in this field a number of unexplained details remain, so that there is an extensive field still open to future research.

Racemoids may be separated into optical isomers in three principal ways, and all three were discovered by Pasteur, viz.,

1. Fission by spontaneous crystallization of the antipodes from the racemoid.

2. Fission by combining the racemoid with optically active compounds.

[1] L. Maquenne, *Ann. chim. phys.*, (6) 29, 271 (1893). G. Tanret, *Compt. rend.*, 109, 908 (1899).

[2] F. M. Jaeger, *Principle of Symmetry*, p. 263, 2nd Edition (1920).

3. Fission by the aid of living organisms attacking the components of the racemoid in a different way.

We shall consider each of these methods in order.

Fission of Racemoids by Spontaneous Crystallization.

This is the way in which Pasteur discovered, in 1848, the existence of *d*- and *l*-tartaric acids, while studying the sodium ammonium salt of racemic acid. If a solution of the racemate is allowed to evaporate slowly at lower temperatures, there are deposited, not the crystals of the racemate, but a mixture of *d*- and *l*-tartaric acid crystals which may be selected and sorted according to their enantiomorphous forms. The corresponding *dextro*- and *levo*-rotary acids can then be obtained from the respective salts.

The question naturally occurs: Why cannot this method be followed in every case where a separable racemoid is present? The answer is, that the possibility of such a fission depends on conditions of temperature, pressure and other factors in such a way, that the equimolecular mixture of the *d*- and *l*-components must have a greater stability, within the range of temperatures and pressures considered, than have the corresponding racemoids. Since "metastable" phases have a greater solubility than the stable ones at the same temperature or pressure, the antipodes must be less soluble than is the racemoid under the conditions prevailing.

Let us consider these relations more in detail.[1] In Figures 18a and 18b are shown graphically the solubilities —*i.e.* concentration of the saturated solutions—of the antipodes and the racemoids under a constant pressure of, say, one atmosphere, for temperatures t_1, t_2, etc.

In the graphs the axis OD indicates the solubilities of the *dextro*-rotary antipode, *i.e.* concentrations of saturated solutions of this antipode at temperatures t_1, t_2, are repre-represented by the vectors OS'_D, OS''_D; the axis OL similarly represents the solubilities of the *levo*-rotary antipode at corresponding temperatures. As these solubilities are equal, at the same temperatures, for both antipodes, then $OS'_D = OS'_L$, $OS''_D = OS''_L$, and so on. In Figure 18a,

[1] H. W. Bakhuis Roozeboom, *Z. physik. Chem.*, 28, 494 (1899).

if at the temperature t_1 some of the *levo*-rotary antipode is added to the saturated solution OS'_D of the *dextro*-rotary compound, the *levo*-rotary antipode is dissolved and diminishes the solubility of the *dextro*-rotary component somewhat, while the excess of the *dextro*-rotary salt is precipitated. The specific rotation of the new solution also is decreased somewhat, but it remains *dextro*-rotary. The curve S'_Dm may represent the solubility curve of the *dextro*-rotary antipode at t_1, if more and more of the *levo*-rotary component is added gradually. At m the solution has become optically inactive because it contains equal amounts of the *d*- and *l*-antipode; at t_1 this solution m is saturated with both components simultaneously and these therefore are in constant contact with the solution, being mixed in equal quantities. In the same way S'_Lm is the solubility curve at t_1 for the *levo*-rotary component, and it has the same shape as S'_Dm. All optically inactive saturated solutions are located on OI. On the one side of this line all points represent more or less *dextro*-rotary saturated solutions, while on the other side they represent more or less *levo*-rotary saturated solutions. If the temperature rises to t_2, Figure 18a represents the solubility curves by S''_DP and S''_LP. When the composition of the saturated solution has become P or P′, respectively, it will be noted that on the addition of *levo*- or *dextro*-rotary components, respectively, crystals of the racemoid are deposited simultaneously with the *d*- or *l*-component. Thus the solutions P and P′ are in equilibrium with a mixture of *d*+racemic or *l*+racemic crystals. The gradual addition of more of the active components causes more of the racemoid to be formed; this accumulates at the bottom of the vessel in gradually increasing quantity until finally the point r of the solubility curve PrP′ is reached, the optically inactive liquid now being in equilibrium with the racemic compound alone. Therefore, if the solubility curve of the pure racemic compound be PrP′ it intersects the curves of the antipodes at P and P′ and these points represent the only optically-active saturated solutions that can be in equilibrium simultaneously at t_2, either with racemoid + *d*-antipode or with racemoid + *l*-antipode. The curve PrP′

contains all *dextro-* or *levo*-rotary solutions that are in equilibrium with the pure racemic compound in the solid phase. The point r is the only optically inactive solution that can be in equilibrium with the racemoid as the solid phase. If S'_DP and S'_LP' are prolonged they intersect at x, which represents an optically inactive saturated solution in contact with a mixture of equal quantities of *d-* and *l*-antipodes as solid phases. It is clear that the solubility at x is greater than that at r; therefore the solution x is supersaturated with respect to the racemoid. It is metastable with

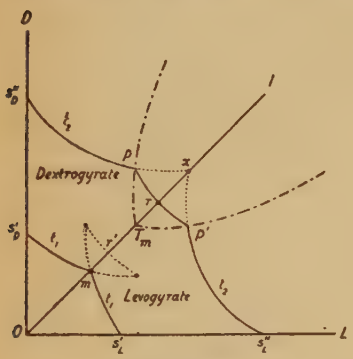


FIG. 18a

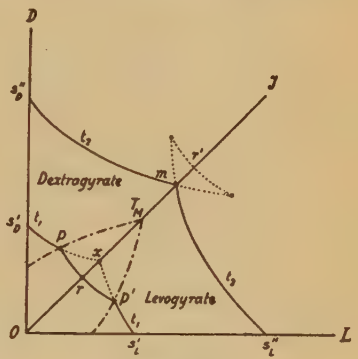


FIG. 18b

respect to r, so that the mixture $d+l$ will automatically be transformed into the racemoid r. Evidently beyond T_m the field of existence of the racemoid gradually increases; below T_m it is only mixtures of $d+l$-antipodes that are the stable solid phase in contact with the solutions. At T_m itself the racemoid and the mixture $d+l$ have the same stability as solid phases in contact with the liquid. Figure 18b represents the conditions where the concentration-trajectory, along which the racemic compound is the more stable solid phase with respect to a mixture of $d+l$, gradually shrinks as the temperatures increase. Above the temperature T_M the racemoid can, at the pressure considered, no longer be the stable solid phase; for increasing temperatures the solubility curves are of the type t_2, where $d+l$ is the stable solid phase in equilibrium with the saturated solutions. For instance, it is easily seen that at t_2 the race-

mic compound as solid phase is metastable with respect to the mixture $d+l$, because r′ would be the solubility of the racemoid at that temperature and this solubility is greater than m. Therefore the field of existence of the racemic compound as a stable solid phase in contact with the solution is cut off abruptly at the temperature T_M which here has the character of a maximum temperature of existence for the racemoid. T_M is the transition temperature (maximal) of the racemoid under a pressure of one atmosphere and it varies in a definite way with the pressure. Evidently at T_M we have the reaction $r \rightarrow d+l$ and the racemoid is transformed into a mixture of the antipodes when heat is added, or the mixture is transformed into the racemic compound when heat is subtracted. According to the law of mobile equilibrium, a maximum transition temperature occurs where there is an endothermic transition of the racemic compound into the mixture of the antipodes. Below T_M the racemic compound crystallizes out of optically inactive solutions; above T_M a mixture of right- and left-handed crystals of the antipodes is deposited from the solution (spontaneous crystallization). In Figure 18a precisely the opposite case was considered. There T_m is a minimal transition temperature for the racemoid, this being only the stable solid phase in equilibrium with the inactive solutions at temperatures above T_m. Of course the heat effect accompanying the transformation of $r \rightarrow d+l$ must here be exactly the opposite to what it was in the previous case.

It is worth while to remember here that Figures 18a and 18b represent vaporless conditions at a pressure of one atmosphere. Although only four phases in a three-component system are present, viz., solid *d*-antipode, solid *l*-antipode, solid racemoid and saturated solution, yet the equilibrium in T_m or T_M is non-variant, according to Gibbs' phase rule, because the external pressure p is fixed beforehand.[1]

[1] The system *d*-antipode, *l*-antipode and the solvent, is a ternary system. An equilibrium of four phases therefore is mono-variant. But if the pressure p is previously fixed, that equilibrium becomes non-variant. An equilibrium of five phases, however, is absolutely non-variant (quintuple point). Therefore the system under its own vapor pressure can exist only at a single definite temperature and a single characteristic pressure.

If the external pressure is allowed to vary, however, then T_m and T_M also will vary with it as long as only four phases are simultaneously present—just as the boundary curves PT_mP' and PT_MP' also vary. As soon, however, as there is a gaseous phase present in equilibrium with the solution, we have five phases simultaneously; in this case the equilibrium is unique and absolutely non-variant, so that there is only one temperature T_u and one special vapor pressure p_u at which the said equilibrium will be possible.

Certainly it is now clear that the solubility-determination of racemoids and antipodes enable one to conclude whether there is a transition temperature for the racemoids and whether it is a minimum or a maximum one. We shall see later on that this has been done, for instance, for potassium trioxalato-cobaltiate and tri[cyclopentylenediammino]-rhodium perchlorate. The possibility of resolving a racemoid into its antipodes by spontaneous crystallization thus depends—disregarding other circumstances—on whether or no the transition temperature at ordinary pressure is located within the field of the usual laboratory temperatures, and whether one is working at temperatures such that the optically active antipodes are the least soluble solid phases compared with the racemoid.

For discussion of the more complicated cases of partial racemism with its possible "transition temperatures," as well as other factors that can impede a fission of a racemoid, the reader is referred to the literature.[1]

It is now apparent that Pasteur's case of sodium ammonium racemate is evidently that of Figure 18a. Here there is a minimum transition temperature $T_m = 27.2°$ at a pressure of one atmosphere, below which the inactive solution deposits a mixture of the *d*- and the *l*-tartrates, according to the following equation:[2]

$$d\text{-tartrate } (+4H_2O) + l\text{-tartrate } (+4H_2O) \overset{2.72°}{\rightleftarrows} \text{racemate } (+1H_2O) + 7H_2O - W_{cal.}$$

[1] See F. M. Jaeger, *Principle of Symmetry*, p. 209–213; 221–223 (2nd Edition, 1920),

[2] J. H. van't Hoff and collab., *Z. physik. Chem.*, 1, 173 (1887); 17, 49, 505 (1895); *Vorlesungen über Spaltung u. Bildung von Doppelsalzen*, p. 81 (1897); *Vorlesungen über Theoretische u. Physikalische Chemie*, v. 2, p. 100 (1899); W. Meyerhofer, *Gleichgewichte der Stereo-isomeren* (1906).

Quite analogous to this case is that of potassium sodium racemate ($+3H_2O$), where the minimum transition temperature is $-6°$.[1] In the case of the rubidium racemate ($+2H_2O$), however, there is a maximum transition temperature of 40.4° according to the equation:

$$\text{racemate}\,(+2H_2O) \overset{40.4°}{\rightleftarrows} d\text{-tartrate} + l\text{-tartrate} + 4H_2O - W'_{cal}$$

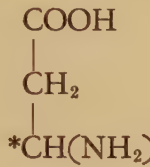
Such transition temperatures can be determined in several ways: by the dilatometric method, which uses changes in specific volume of both systems; by tensimetrical methods in the case of hydrated salts or volatile compounds; or by solubility determinations. Most laboratory work has been done by the latter method because it is a relatively simple one. It has given good results, for instance in some cases in establishing the occurrence of spontaneous crystallization in complex salts. The tensimetrical method has readily been applied in the study of the tartrates mentioned.

Although the relations between antipodes and racemoids now seem to be perfectly clear, experience teaches that many troublesome difficulties remain. If thermodynamics tells us the stability relations between several phases under certain conditions, this only means that under these conditions such more stable phases may be reasonably expected to appear, but not that they must occur. The appearance of a new phase depends on many circumstances that cannot be foreseen, for the simple reason that we know almost nothing about them. In this case also experience teaches that optically active forms may often appear under temperature conditions at which, from the thermodynamic point of view, they are undoubtedly metastable with respect to the racemic compound from which they arise.

Gernez[2] was the first to find instances of this kind. He drew attention to the remarkable fact that if a small crystal of either component or of an isomorphic or isodimorphic substance, be introduced into the optically inactive supersaturated solution, the excess solute will often be deposited in the form of one of the components only,

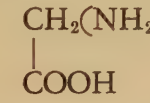
[1] D. Gernez, *Compt. rend.*, 63, 843 (1866).
[2] D. Gernez, *loc. cit.*

even in those cases where the racemoid is the stable phase. Purdie[1] subsequently found this to be true in the case of zinc ammonium lactate. Ostromisslensky[2] made a systematic study of these phenomena. He found, for instance, that if a supersaturated solution of sodium ammonium racemate at 6° were inoculated with a crystal of *levo*-



l-*Asparagine*

asparagine, there was deposited only the *dextro* tartrate. It is very remarkable, also, that substances having no rotatory power can produce this effect. Thus from a supersaturated solution of inactive asparagine he obtained only the one kind of component on inoculating the liquid with a nucleus of the inactive hemihedral crystal of glycocoll,



Ostromisslensky's work needs to be extended and rechecked, however, because he describes a number of phenomena that still appear hazy.

We found that in the case of the complex tri[cyclopentylenediammino]-cobaltic perchlorate, the optically inactive solutions of the anhydrous racemoid usually deposited the crystals of the antipodes ($+12H_2O$) at temperatures where the racemic compound is undeniably the stabler phase.[3] Werner[4] observed that one of the components exclusively could be precipitated from inactive solutions at temperatures where the antipodes were the stabler phase, if to the supersaturated solution there be added a mixture of al-

[1] T. Purdie, *J. Chem. Soc.*, 63, 1143 (1893).
[2] Ostromisslensky, *Ber.*, 41, 3035 (1908).
[3] F. M. Jaeger and H. B. Blumendal, *Z. anorg. Chem.*, 175, 167 (1928).
[4] A. Werner, *Ber.*, 47, 1955, 2171, 2179 (1914).

cohol and ether, provided only a slight excess of the desired antipode be present. All such phenomena still need systematic experimental study before they will be fully explained and completely understood. There is, here, a wide field still open for investigation. We shall consider it in more detail later on.

The fission of racemoids into optically active components by spontaneous crystallization does not occur in the majority of cases. One must have recourse, therefore, to one of the other methods devised by Pasteur. We shall take these up in detail in the next chapter.

Fission of Racemoids by Means of Optically Active Compounds.

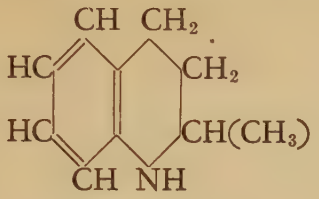
Nature furnishes, in the cells and organs of plants and animals, a number of substances there present in the state of one single optically active antipode, the other antipode being absent. Such natural optically active bases or acids can be used, as Pasteur showed in a number of cases, to obtain the antipodes from a racemic compound.

The principle of this method is as follows. Suppose any racemoid R be composed of its antipodes A_D and A_L. Both antipodes possess the same scalar properties, *e.g.* the same solubilities at every temperature. A natural optically-active substance, C, may be of such chemical character that it can combine with A_D or A_L; also C is supposed to differ from its (often unknown) mirror image C′. If combination takes place we obtain substances A_DC and A_LC which are no longer each other's mirror images; for the mirror image of A_DC would be A_LC' and that of A_LC would be A_DC'. Therefore A_DC and A_LC no longer have equal scalar properties, *e.g.* solubilities, and may be separated from each other by fractional crystallization if the difference in solubility is sufficiently great. We may obtain A_DC and A_LC separately in this way, and after removing C the antipodes A_D and A_L may be obtained in a pure state.

Pope and Peachy[1] have proposed a useful variation of this method for that case, where the difference in solubility is not sufficiently great. They found a case of this kind, for

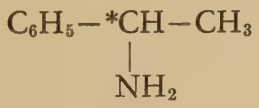
[1] W. J. Pope and S. J. Peachy, *J. Chem. Soc.*, **75**, 1066 (1899).

example, when trying to separate tetrahydroquinaldine by means of *dextro*-rotary bromocamphorsulphonic acid,

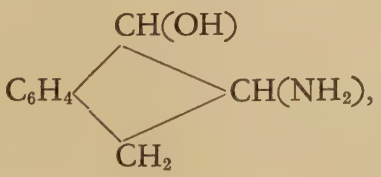


Tetrahydroquinaldine

$C_{10}H_{14}BrO.SO_3H$. They added only one molecule (half the necessary amount) of ammonium-*d*-bromocamphorsulphonate to two molecules of tetrahydroquinaldine hydrochloride. In this case the less and the more soluble compounds of the antipodes of the base with *d*-bromocamphorsulphonic acid as well as ammonium chloride, NH_4Cl, will be formed, a part of both antipodes remaining in solution as hydrochlorides. On slowly evaporating the solution more and more of the less soluble compound gradually separates out, the equilibrium being restored at each precipitation by the formation of a new quantity of the less soluble *d*-bromocamphorsulphonate of the corresponding antipode, until the other alone remains in the solution as hydrochloride. This is a very convenient procedure in many cases. The method described above is the one most generally employed in the laboratory. For securing the fission of racemic acids, one uses such natural optically active bases as cinchonine, quinidine, cinchonidine, quinine, yohimbine, brucine, strychnine, and morphine; and recently synthetic bases also, such as *d*-α-phenylethylamine:

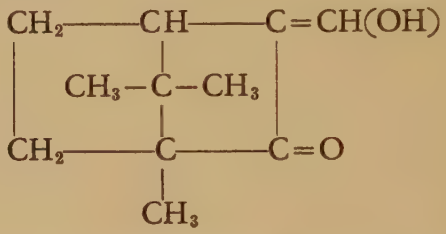


hydroxyhydrindamine,



and the like. On the other hand the fission of racemic bases are often obtained by means of such natural optically active acids as *d*-tartaric acid, and *l*-malic acid; or with the aid of such synthetic acids as *d*- and *l*-camphorsulphonic and *d*-bromocamphorsulphonic acid, or α-nitrocamphor, $C_{10}H_{15}O(NO_2)$.

In many cases the separation of racemic bases is conveniently accomplished by condensation with *d*-hydroxymethylenecamphor,



which is subsequently split off again and the activated base regenerated.[1]

Of course the newly obtained optically active components of synthetic bases or acids can, in their turn, be used later on for the fission of other racemic acids or bases. The method is of universal application; but in every case one meets the difficulty of making a suitable choice from among the optically active substances at hand, in order to secure a sufficiently great difference in solubility between the resulting compounds. Moreover suitable conditions of crystallization of these products also play a preponderant rôle and the experimenter often meets numerous and serious obstacles in establishing them.

Another difficulty may arise at this point due to the undesired formation of so-called partial racemoids.[2] Such cases are characterized by the special circumstance that the optically active base or acid combines with the racemoid as a whole; the resulting compound can be recrystallized without breaking up into its components, but the latter now are no longer each other's mirror images. The partial racemoid can be separated into its components only

[1] W. J. Pope and J. Reed, *J. Chem. Soc.*, 103, 451 (1913).
[2] H. W. Bakhuis Roozeboom, *Z. physik. Chem.*, 28, 502 (1899).

if there is a maximal or minimal transition temperature for it, just as in the case of true racemoids. In this case the components have different solubilities, the graphs representing the relations are analogous to those in Figure 18; but they serve to show that the symmetry of the whole figure is lost. The phenomena to be expected here may be deduced from the figure in the same manner as before. In this case also the transition temperature of the partial racemoid often is too far away from the temperatures of the experiment to permit fission in this manner. Ladenburg[1] observed instances of this kind in the case of strychnine racemate, where a maximum transition temperature of 30° is present, and in the case of quinine methylsuccinate. A maximum transition temperature of 50° is observed with brucine biracemate. Numerous instances of this impeding phenomenon are now recorded in the literature.[2]

Fission of Racemoids by Means of Living Organisms.

The third method developed by Pasteur[3] employs those living organisms, bacteria, moulds and yeasts, and some of those complicated proteïds called ferments or enzymes.

The method is based upon the experience that such lower organisms appear to attack one only of the antipodes which they use for food, and leave the other intact as being unsuited for their physiological needs. Fischer and others have found the same fact in studying the action of yeast in the fermentation of sugars.[4] These selective activities have already been a frequent subject of study[5] and their explanation seems to lie in the great difference in the speed of reaction of the organisms or enzymes on the two enantiomorphous molecules. The method is not often applied, however, because of the great disadvantage that half of the material is consumed by the process. As we shall not have occasion to use it in the cases to be discussed here-

[1] A. Ladenburg, *Ber.*, 27, 75 (1884); 31, 524, 937, 1969 (1898); 36, 1649 (1903); 40, 2279 (1907); etc.

[2] See F. M. Jaeger, *Principle of Symmetry*, p. 221 f, (2nd Edition 1920).

[3] L. Pasteur, *Compt. rend.*, 32, 110 (1851); 36, 26 (1853); 37, 110, 162 (1853); 51, 298 (1860).

[4] E. Fischer, *Ber.*, 37, 2031, 2985, 3228, 3479 (1894); 28, 1429, 1508, 3031 (1895).

[5] C. Neuberg, *Biochem. Z.*, 18, 431 (1904); H. Pringsheim, *Z. physiol. Chem.*, 65 96 (1910).

after I shall not go into detail concerning it, although there is much work yet to be done in this direction.

It must be remarked, however, that the whole topic is of the greatest interest both because of its connection with the different physiological actions of optically active antipodes in general,[1] and because of the explanation of them offered by Pasteur and many other workers.

Natural and artificial Synthesis of Optically Active Matter.

There remains to be discussed a question in connection with the contrast between two enantiomorphous substances. On attempting a laboratory synthesis of dis-symmetrically arranged molecules, starting from optically inactive substances, experience has taught us that we always obtain optically inactive materials such as racemoids, which must then be separated into the optically active antipodes by one of the methods just described. The reason for this is that the two enantiomorphously related configurations of the antipodes have similar mechanical stability, because they are formed under the influence of the same directional forces. They have, therefore, the same chance to be formed and the final product always consists of the same number of right- and left-hand molecules.

In striking contrast with this experience is the fact, pointed out by Pasteur, that in by far the larger number of cases only optically active molecules—one of the two possible antipodes—are met with in the living cells of plants and animals. This fact makes it appear that, notwithstanding the very great development of organic synthesis, a deep gulf yet remains between natural and artificial synthesis. On the other hand, experience has shown that laboratory experiments may also yield optically active derivatives from reactions in which the primary reactants are themselves optically active. The previous presence of dissymmetrical molecules appears to have, therefore, an undoubted directional influence in so far as their presence causes the reaction to favor the formation of one of the two possible dissymmetrical isomerides. The conclusion is obvious, that the one-sidedness of natural synthesis is also

[1] For the literature on this subject, see F. M. Jaeger, *op. cit.*, p. 224–228.

due to the preliminary presence in the living cell, of other optically active substances which exert a directional force upon the syntheses taking place therein. In the light of the numerous investigations during the past ten years by Marckwaldt, McKenzie, Bredig and others, on such so-called "partial asymmetric synthesis" there can be no doubt of the correctness of this view.

The contrast between natural and artificial synthesis may be said to have disappeared to the following extent: the chemical forces acting in the living cell and in the test tube are the same, but the circumstances are different—natural synthesis is always taking place under the directional influence of optically active molecules already present in the cells. Their reaction chains are one-sided through hereditary succession during numberless ages of evolution in plant life. But then arises the question: How was the first optically active substance in the living cell, which started the whole series of subsequent one-sided syntheses, formed from such optically inactive materials as carbon dioxide, water and ammonia? In contrast to the "partial" asymmetrical synthesis, this problem is commonly called that of the "total asymmetric synthesis" of optically active molecules starting with optically inactive materials.

Pasteur reflected on this problem and made some unsuccessful experiments to influence synthesis in vegetable cells by external influence. It is evident that, at one time or another, there must have been external dis-symmetrical forces influencing the synthetic process for a limited time, in such a manner that one of the optically active antipodes was generated in excess. In later years there have been many experimental attempts to execute such a total asymmetric synthesis under the influence of externally applied dis-symmetrical forces of a different nature. Some students have applied superimposed magnetic and electric fields; others have used photosynthetic processes employing right- or left-handed circularly polarized light of selected wave length. So far all these experiments have remained unsuccessful; the problem of "total asymmetric synthesis" is still unsolved.

We have tried to show,[1] for example, that there is a difference in the reaction-velocity when optically active potassium oxalato-cobaltiate is decomposed under the action of right- or left-handed circularly polarized light, with a resulting production of oxalato-cobaltoate and the evolution of carbon dioxide. Even in this case of very strongly rotating molecules, there were no determinable differences in velocity within the limits of experimental error. Yet there must have been a cause of this kind; sunlight reflected at the surface of the ocean is always partially polarized elliptically or circularly under the influence of the terrestrial magnetic field. It is, therefore, surely only a question of finding the suitable materials and experimental conditions, to realize again such an action.[2]

The necessary conditions will be that the externally applied forces are a *conditio sine qua non* for the initiation of the reaction which would be impossible without them. Furthermore, these external forces must be of a symmetry[3] sufficiently low to form a system of directional forces different from its mirror image. This is the case with circularly-polarized light of a certain direction, with linearly-polarized light when rotated by a magnetic field, with superimposed magnetic and electrical fields having their lines of force mutually parallel. Perhaps we shall have the best chance of inventing photochemical processes of a suitable character and subjecting the substances to circularly-polarized light of the proper wave-length—say when demonstrating the differences in the speed of reaction—if we start with one of the antipodes; or select reactions in which, under the influence of light, an asymmetric carbon atom in the sense of LeBel-van't Hoff's theory is produced in the newly generated molecule. It is only by trying experiments of this kind that the problem can be solved and we return to this question in Chapter XIII.

[1] F. M. Jaeger and G. Berger, *Rec. trav. chim.*, 40, 153 (1921); and unpublished results.
[2] A. Byk, *Ber.*, 37, 4696 (1904); *Z. physik. Chem.*, 49, 641 (1905).
[3] Concerning the symmetry of physical causes and effects, see F. M. Jaeger, *Principle of Symmetry*, pp. 89 ff. and 316 ff. (2nd Edition 1920).

CHAPTER V

Chemical Structure of Complex Inorganic Salts.

It is now time to take up that special field of research to which we shall apply the principles set forth in the foregoing, namely, the field of the complex inorganic salts. I shall start by briefly reviewing the theoretical views concerning the chemical structure of these remarkable compounds, and the reasoning on which our concepts of their spatial architecture are founded. We owe most of the reasoning to Werner, whose brilliant researches on complex salts, carried through many decades, furnished him with the final and indubitable proof of the correctness of his views concerning the spatial arrangement of their constituents. We may start with a series of simple facts that will briefly explain the foundations of Werner's reasoning.

When one passes a current of air through a solution containing cobaltous chloride, $CoCl_2$, ammonium chloride, NH_4Cl, and free ammonia, NH_3, it is found possible to isolate from the oxidized solution two salts of trivalent cobalt, both containing ammonia and having the empirical composition $CoCl_3 + 6NH_3$ and $CoCl_3 + 5NH_3$, respectively. Making the same experiment when the ammonium chloride is replaced by ammonium carbonate in large excess, one obtains another salt containing Co, Cl, CO_3, and ammonia, which after treating at low temperatures with cold concentrated hydrochloric acid yields a product having the empirical composition $CoCl_3 + 4NH_3$. When one compares the properties of these three salts—each of which may be regarded as derived empirically from its predecessor by the successive loss of a single molecule of ammonia—very striking differences are at once evident. Externally they differ remarkably in color, that is, as to their absorption spectra both in the solid state and in

solution. The chloride having $6NH_3$ is orange-yellow (luteo-salt), the one with $5NH_3$ is bluish-red (purpureo-salt), and that having $4NH_3$ is emerald green (praseo-salt). Such differences in color usually indicate intrinsic differences in the linkage of the atoms within the molecules. In the present cases this is confirmed by the fact that, on adding a solution of silver nitrate to their respective cold solutions, there are at once precipitated in the form of AgCl three chlorine atoms from the $6NH_3$ salt, only two chlorine atoms from the $5NH_3$ salt, and but a single chlorine atom from the $4NH_3$ salt; the remaining chlorine atoms of the last two cases are evidently much more firmly held than the others. Cryoscopic determinations of the apparent molecular weights, measurements of the molecular electrical conductivity, etc., prove that the first salt, when in solution, is a quarternary, the second a ternary, and the third a binary electrolyte; so that their behavior can be represented schematically by formulas as follows:

$$\{Co^{III}(NH_3)_6\}Cl_3;\ \left\{\begin{matrix}Co^{III}(NH_3)_5\\ Cl\end{matrix}\right\}Cl_2;\ \left\{\begin{matrix}Co^{III}(NH_3)_4\\ Cl_2\end{matrix}\right\}Cl$$

The chlorine atoms outside the braces are those that are ionogenic and therefore are precipitated immediately in the form of AgCl. Their solutions do not contain appreciable quantities of free Co^{III} ions or free ammonia. According to Werner, they must be considered as chlorides of complex ions which in the three cases mentioned, are respectively tri-, bi-, and monovalent cations:

$$\{Co^{III}(NH_3)_6\}^{\cdots},\ \left\{\begin{matrix}Co^{III}(NH_3)_5\\ Cl\end{matrix}\right\}^{\cdot\cdot},\ \left\{\begin{matrix}Co^{III}(NH_3)_4\\ Cl_2\end{matrix}\right\}^{\cdot}$$

In all these cases the existence of such complex ions in solution has been confirmed by the usual physico-chemical methods, such as migration measurements or determining molecular conductivity in solution. The further properties of these three salts are in full agreement with this supposition.

A similar behavior is observed in the case of the ammonia compounds of tetravalent platinum studied by

Werner.[1] The terms of this series are as follows:

$$\{Pt^{IV}(NH_3)_6\}Cl_4;\ \left\{\begin{matrix}Pt^{IV}(NH_3)_4\\ Cl_2\end{matrix}\right\}Cl_2;\ \left\{\begin{matrix}Pt^{IV}(NH_3)_3\\ Cl_3\end{matrix}\right\}Cl;$$

$$\left\{\begin{matrix}Pt^{IV}(NH_3)_2\\ Cl_4\end{matrix}\right\};\ \left\{\begin{matrix}Pt^{IV}(NH_3)\\ Cl_5\end{matrix}\right\}K;\ \{Pt^{IV}Cl_6\}K_2.$$

The molecular electrical conductivity of these salts decreases from 522.9 ohm^{-1} for the first salt, to 228 ohm^{-1} for the second, and 96.7 ohm^{-1} for the third, becoming practically zero for the fourth salt. The complex cation which carries four positive charges in the first salt, becomes bivalent in the second and monovalent in the third salt; but in the fifth salt the cation changes to a monovalent and in the sixth salt to a bivalent anion. Now the molecular conductivities of the corresponding potassium salts show values of 108 ohm^{-1} and 256 ohm^{-1} respectively:

$$\{Pt^{IV}(NH_3)_6\}^{\cdots\cdot},\ \left\{\begin{matrix}Pt^{IV}(NH_3)_4\\ Cl_2\end{matrix}\right\}^{\cdot\cdot},\ \left\{\begin{matrix}Pt^{IV}(NH_3)_3\\ Cl_3\end{matrix}\right\}^{\cdot},$$

$$\left\{\begin{matrix}Pt^{IV}(NH_3)_2\\ Cl_4\end{matrix}\right\},\ \left\{\begin{matrix}Pt^{IV}(NH_3)\\ Cl_5\end{matrix}\right\}',\ \{Pt^{IV}Cl_6\}''.$$

The fourth salt of this series shows no appreciable conductivity in solution and evidently forms no ions; its behavior reminds one of the non-ionizing organic compounds.

In all such cases as the above, the complex ion consists of a central metallic multivalent atom surrounded by six substituents. If the latter are themselves electrically neutral molecules, *e.g.* water, ammonia, or pyridine, then the complex ion has the same charge as the central atom. If these molecules, however, be successively replaced by chlorine atoms the charge of the complex ion appears to be diminished, with each replacement, by as many units as there are negative chlorine atoms in the layer of substituents about the central metallic atom. Werner calls this characteristic number of six substituents, occurring in the case of the trivalent cobalt atom as well as in that of the tetravalent platinum atom, the "co-ordination number" of the atom, and it appears from experience to be independent

[1] A. Werner, *Z. anorg. Chem.*, 3, 267 (1893); 8, 153 (1895); A. Werner and A. Miolati *Z. physik. Chem.*, 12, 35 (1893).

generally of the particular valency of the central atom. The value six is very often met with as a co-ordination number; for example in the case of the complex anions of potassium ferrocyanide, $\{Fe^{II}(CN)_6\}''''$, and potassium ferricyanide, $\{Fe^{III}(CN)_6\}'''$, where the central atom of the ion is bi- and trivalent respectively. Other co-ordination numbers than six may occur, even with the same metal; thus in the case of bivalent platinum we have complex salts of the types:

$$\{Pt^{II}(NH_3)_4\}Cl_2;\ \left\{\begin{matrix}Pt^{II}(NH_3)_3\\ Cl\end{matrix}\right\}Cl;\ \left\{\begin{matrix}Pt^{II}(NH_3)_2\\ Cl_2\end{matrix}\right\};$$

$$\left\{\begin{matrix}Pt^{II}(NH_3)\\ Cl_3\end{matrix}\right\}K;\ \{Pt^{II}Cl_4\}K_2.$$

The co-ordination number in this case appears to be four. Often, but by no means always, the co-ordination number appears to be twice the valency of the central atom, sometimes thrice.

Without taking up the full details of the many questions or corollaries connected with Werner's co-ordination theory, it simply may be stated that in general the co-ordination number indicates the maximum number of substituents that can find a place immediately about the central metallic atom, being as it were intercalated between this and the ionogenic anions or cations. They are arranged in what Werner distinguishes as the "primary shell"; in our case this contains six ammonia groups. Suspicion arises, therefore, that this co-ordination number is in some way connected with certain spatial relations existing about the central atom. Here, as in the chemistry of organic compounds, the occurrence of isomers among these complex salts has been the starting point of all considerations regarding the spatial architecture of such complex ions. In the beginning Werner made this supposition of a stereometric arrangement of substituents about the central atom, and this was confirmed later by experiments in a very striking manner, as we shall see.

The repeated occurrence of the co-ordination number 6 among the complex salts, led Werner to suppose that if all six substituents were identical they were placed about the central atom essentially at the corners of a regular octahedron having the central atom at its center. Varied and

extensive experience has plainly confirmed this view. Moreover it seems that even if the substituents are not identical, there is but a relatively slight distortion of the whole configuration from a true octahedral arrangement. We shall take up in detail later on, the special case where the co-ordination number is four. At present the important case for our immediate purposes is the one where the co-ordination number is six, and we shall consider this.

First let us inquire into the consequent possible occurrence of isomers due to supposing an octahedral arrangement of the six substituents about the central atom.

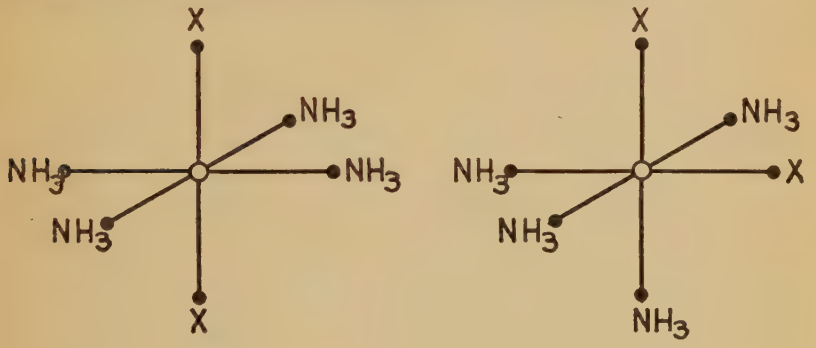


FIG. 19

If, in the complex ion $\{Co^{III}(NH_3)_6\}\cdots$, one of the ammonia molecules be replaced by a substituent X, it is evident that no isomer can occur, it making no difference which of the six ammonia molecules is replaced by X. However, if two ammonia molecules be replaced by two like substituents X, then we may distinguish the two different cases shown in Figure 19.

In the first or *trans*-position both substituents X are as far apart as possible, being placed on either side of the plane passing through the remaining four ammonia molecules. In the second or *cis*-position, they are placed as near each other as possible, being located at the ends of the same octahedral edge. Indeed experience teaches that in this case we can obtain two isomers with each complex salt of this type. Thus if X is a (NO_2) group we get two series of dinitro-tetrammino-cobaltic salts: the orange-

yellow croceo-salts (obtained by Gibbs in 1875) and the yellowish brown flavo-salts (obtained by Jörgensen in 1894), of which the first have both (NO_2) groups in the *trans* position and the second have them in the *cis* position. The substituents X may also be true nitrito groups (O–NO); and here again two isomeric series of salts are obtained, namely, reddish-brown *cis*-salts and analogously constituted yellowish-red *trans*-salts. If X is a chlorine atom two series of isomeric salts also are obtained: the emerald green praseo-salts having both chlorine atoms in the *trans* position, and the bluish-violet violeo-salts where they are in the *cis* position. Werner's experimental work completely explains the true constitution of these isomers and their mutual relations. All the facts are plainly in agreement with the theoretical views mentioned above.

I do not wish to consider here the details of the question as to how the co-ordinated groups or atoms in the primary shell of these complex ions are linked to the central atom, nor how the ionogenic atoms or radicals outside the complex ion are linked to it. No doubt the linkage of the six NH_3 groups of the primary shell of the hexammino salts to the cobalt atom is effected by residual affinities of the trivalent nitrogen atom—a certain amount of binding-energy being needed to keep each NH_3 molecule in its proper place within the space surrounding the metallic central atom. We may reserve discussion of these questions for later lectures. I would here draw your attention to some important features concerning the rules for substitution in the six groups surrounding the central atom.

In complex hexammino salts of type $\{Me^{III}(NH_3)_6\}X_3$, each molecule of NH_3 can be replaced by one molecule of H_2O (roseo-salts), by one molecule of a monovalent alcohol or a ketone, or of any other monovalent pseudo-base such as hydroxylamine, pyridine or the like. It may also be replaced by one molecule of an urethane, of urea, of an amide or the like, for example:

$$\underset{(roseo\text{-}salts)}{\left\{\begin{matrix} Co^{III}(NH_3)_5 \\ (H_2O) \end{matrix}\right\}X_3}; \quad \{Cr^{III}(Urea)_6\}X_3;^{1} \quad \{Co^{III}(NH_2.OH)_6\{X_3$$

[1] D. Kalkman and A. Werner, *Ann.*, 322, 302 (1902).

In the case of polyvalent pseudo-bases, like ethylenediamine, propylenediamine or α-phenanthroline, or of polyvalent alcohols like glycol and glycerol, as many NH_3 molecules will be replaced as there are equivalent NH_2 or OH groups active in those substitutes under the conditions prevailing. Thus we know of salts of the types:[1]

$$\left\{\begin{matrix}Co^{III}(Ene)_2\\(NH_3)_2\end{matrix}\right\}Cl_3;\quad \{Co^{III}(Ene)_3\}Cl_3;\quad \{Co^{III}(Glycol)_3\}Br_3;^{2}$$

$$\{Me^{II}(Glycerol)_3\}X_2;\quad \{Fe^{II}(\alpha\text{-Phen})_3\}X_2;^{3}$$

$$\{Fe^{II}(\alpha\text{-}\alpha'\text{-Dipyr})_3\}X_2.$$

The same is true for complex anions of the hexacido type:

$$\underset{\textit{pale yellow}}{\{Co^{III}(CN)_6\}}Me_3;\quad \underset{\textit{greenish-violet}}{\{Cr^{III}(O.CO.H)_6\}}Na_3 + 4\tfrac{1}{2}H_2O;^{4}$$

$$\underset{\textit{deep green}}{\{Co^{III}(C_2O_4)_3\}}Me_3;\quad \underset{\textit{blood red}}{\{Rh^{III}(C_3H_2O_4)_3\}}K_3 + 5H_2O.^{5}$$

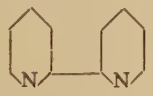
We can also produce mixed substitutions of basic and acid groups or radicals; but these are now accompanied by corresponding changes in the electrical charge of the complex ion, according to the principles stated above. Instances of this kind are:

$$\underset{\textit{green}}{\left\{\begin{matrix}Co^{III}(Ene)_2\\Cl_2\end{matrix}\right\}}Cl;\quad \underset{\textit{red}}{\left\{\begin{matrix}Co^{III}(NH_3)_4\\(CO_3)\end{matrix}\right\}}Cl;\quad \underset{\textit{red}}{\left\{\begin{matrix}Co^{III}(Ene)_2\\(C_2O_4)\end{matrix}\right\}}(NO_3);$$

$$\underset{\textit{purplish red}}{\left\{\begin{matrix}Co^{III}(Ene)_2\\Cl\\(H_2O)\end{matrix}\right\}}(SO_4) + 1\tfrac{1}{2}H_2O.$$

[1] Ene = 1 molecule of ethylenediamine, $NH_2.CH_2.CH_2.NH_2$;

α-Phen = 1 molecule of α-phenanthroline, ;

α-α′-Dipyr = α-α′-dipyridyl,  ; and so on.

[2] A. Grün and collab., *Ber.*, **41**, 3465 (1909); **43**, 1051, 1291 (1911).
[3] F. Blau, *Monatsh.*, **19**, 647 (1898).
[4] R. Weinland and H. Reihlen, *Ber.*, **46**, 3148 (1913).
[5] F. M. Jaeger, *Rec. trav. chim.*, **38**, 300 (1919).

These examples suffice to illustrate the general principles by which the formulas of such complex salts may be deduced.

Finally we may make a few comments on the color of these salts, that is their specific light absorption over the visible portion of the spectrum.

We do not know of any colorless cobalt salts; but it has been proved beyond doubt that such colorless salts do occur with other central metallic atoms; thus platinum, rhodium, and iridium compounds of the hexammino type are colorless, also $Ni(CO)_4$ is a colorless liquid. It is not always possible to predict with certainty and directly the change in color that will take place when certain substituents in a complex ion are replaced by others. In the course of his long-continued researches Werner found that generally an increasingly deeper color is obtained by the consecutive substitution of the elements in the following order:

$$C \rightarrow N \rightarrow S \rightarrow O \rightarrow Cl \rightarrow Br \rightarrow I$$

or better, if radicals are considered:

$(CN;CO); \rightarrow$ (for C) (NO_2), (Ene), (NH_3), $(NCS); \rightarrow$ (for N) $(SO_3); \rightarrow$ (for S)

(OH_2), (ONO), (OAcyl), $(OH); \rightarrow$ halogens. (for O)

For example, in the cobalt derivatives: $\{Co^{III}(CN)_6\}K_3$ is pale yellow; $Co(CO)_4$ is orange red; Co^{III}-N complex salts are yellow to dark brown; the introduction of halogen atoms makes them violet, green, pale red to dark red, and finally reddish-violet. A systematic quantitative investigation of the light-absorbing powers of these complex salts in solution, or as gases if possible (perhaps with some acetylacetonates of metals), would be very important in connection with studies of their true constitution. The scanty data hitherto obtained do not justify any general conclusion regarding the latter.

We may now give more particular attention to the spatial relations characteristic of these substitutions. For

example, what is to be expected if each pair of the six NH_3 groups in the hexammino salts, be replaced successively by one, two, or three molecules of a bivalent pseudo-base, such as the symmetrically constituted ethylenediamine? In the first place, experiment shows that two NH_3 molecules in the *trans* position can never be replaced in this way. Evidently we have, therefore, only to consider the replacing of each pair of NH_3 groups in the *cis* position by one molecule of ethylenediamine. The three possible replacement products of the complex ion thus obtained are, consecutively:

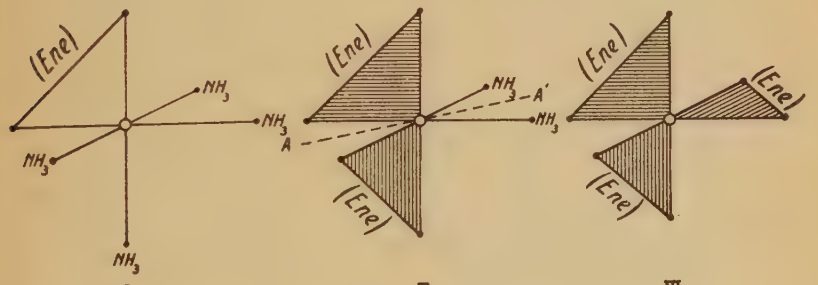
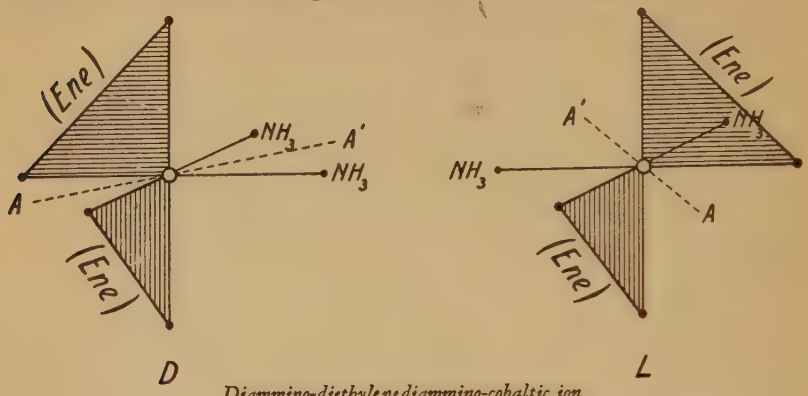


FIG. 20

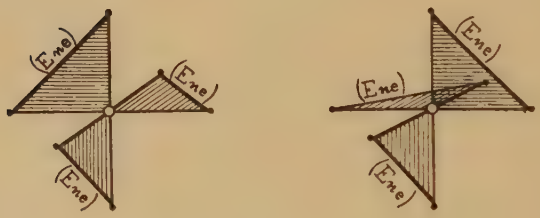
The ethylenediamine molecule, $NH_2.CH_2.CH_2.NH_2$, itself having a highly symmetrical constitution, the ion I (Figure 20) has at least a plane of symmetry passing through the Co atom, the group Ene and two NH_3 molecules, another plane perpendicular to this one, and a polar binary axis which is the intersection of these two planes. Ion II (Figure 20), however, possesses only a single polar binary axis *AA'* passing through the Co atom and bisecting the angle between two NH_3 groups. The ion III (Figure 20) has three polar binary axes passing through the middle of each ethylenediamine molecule, as well as a homopolar ternary axis at right angles to the plane containing the three binary axes. This ion III has the symmetry characteristic of ordinary quartz crystals (D_3). Since ion I has symmetry planes among its symmetry elements, it is superposable on its mirror image; but ions II and III

having only axial symmetry, must differ from their mirror images according to the principles already explained. In fact the ions shown diagramimatically in Figures 21 and 22



Diammino-diethylenediammino-cobaltic ion

FIG. 21



Triethylenediammino-cobaltic ion

FIG. 22

are real mirror images of each other and can never be brought to coincide by any kind of shift. The ions of Figure 22 are shaped like three-bladed right- and left-hand propellers. Therefore all salts of the series:

$$\left\{\begin{matrix}Me^{III}(Ene)_2\\(NH_3)_2\end{matrix}\right\}X_3;\ \left\{\begin{matrix}Me^{III}(Ene)_2\\(C_2O_4)\end{matrix}\right\}X;\ \left\{\begin{matrix}Me^{III}(Ene)_2\\Y_2\end{matrix}\right\}X;$$

$$\left\{Me^{III}(Ene)_3\right\}X_3;\ \text{etc.},$$

must exist in two optically active forms which are resolvable into their antipodes, exactly as in the case of organic compounds. The complete experimental confirmation of

these predicted phenomena furnishes the final proof of the correctness of our suppositions concerning the tridimensional arrangement of the constituents of these remarkable compounds. Once more Pasteur's principle is illustrated to its fullest extent in terms of the modern theory of symmetry. The necessary and final condition for a possible resolution of such compounds into right- and left-hand enantiomorphous isomerides is, not the presence of asymmetrical atoms in the molecule nor the total asymmetry of the configuration of the atoms in space as a whole, but solely the fulfilment of the single condition that the higher or lower symmetry of such spatial arrangements be a purely axial one. This condition is in all cases the sole determining factor for the whole phenomenon of optical isomerism.

The same holds true exactly for similar compounds having complex anions of the hexacido type, or in which cations or anions are present with basic as well as acid substituents. Thus all salts derived from complex ions of the following type:

$$\left\{Co^{III}(C_2O_4)_3\right\}''' ; \left\{\begin{matrix}Co^{III}(C_2O_4)_2\\(NH_3)_2\end{matrix}\right\}' ; \left\{\begin{matrix}Co^{III}(Ene)\\(C_2O_4)_2\end{matrix}\right\}' ;$$

$$\left\{\begin{matrix}Co^{III}(Ene)_2\\(NO_2)_2\end{matrix}\right\}^{\cdot} ; \left\{\begin{matrix}Co^{III}(Ene)_2\\(C_2O_4)\end{matrix}\right\}^{\cdot}$$

are also resolvable into such antipodes. These conclusions have been fully confirmed by experimental evidence.

These manifold facts create a sound basis for the stereochemistry of such salts, even when their complex ions have no organic radicals at all. The stereochemistry of inorganic and organic substances is thus shown to be based upon the same fundamental principles as those governing the phenomena of tridimensional symmetry in general.

CHAPTER VI

Complex Salts of Tri[ethylenediammino] Type

This chapter may start with the discussion of the results of investigations on complex salts of the tri-[ethylenediammino] type,[1] for example:

$$\{Me^{II}(Ene)_3\}X_2;\ \{Me^{III}(Ene)_3\}X_3;\ \{Me^{IV}(Ene)_3\}X_4$$

in which the substituents are three equal molecules of such bivalent bases ase thylenediamine, α-α'-dipyridyl, and α-phenanthroline, which are themselves of highly symmetrical structure, so that they do not occur in optically active forms. By making this simplifying supposition it is possible to avoid complications which we shall have to consider later in connection with some other cases. In general these salts may be regarded as derivatives of cations of the tri[diammino] type.

Since both have the same symmetry relationships, we can consider simultaneously the corresponding results for the complex anions of the tri-oxalato and trimalonato types,[2] or in general of the tri-biacido type:

$$\{Me^{III}(C_2O_4)_3\}'''; \{Me^{III}(C_3H_2O_4)_3\}'''.$$

In this case also the substitutes are so built that they themselves can not exist as optically-active antipodes.

Let us begin with the salts of the tri[diammino] type of this kind.

Ethylenediamine ($NH_2.CH_2.CH_2.NH_2$) is a base having a very strong tendency to combine with metallic salts

[1] A. Werner, *Ber.*, **45**, 121, 433, 865, 1228 (1912); A. Werner and P. Smirnoff, *Helv. Chim. Acta*, 3, 482 (1920); A. Werner, *Festschrift, Naturf. Gesell. Zurich*, 553 (1917); F. M. Jaeger, *Rec. trav. chim.*, 38, 171–241 (1919); *Z. Krist.*, 58, 172 (1923); where further references are given to other literature on this subject.

[2] A. Werner, *Ber.*, **45**, 3061 (1912); 47, 1954 (1914); F. M. Jaeger, *loc. cit.*, 212–314; M. Délépine and G. Bruhat, *Bull. soc. chim.*, (4) **21**, 157 (1917); W. Thomas, *Trans. Chem. Soc.*, **119**, 1140 (1921); E. Wahl, *Ber.*, **60**, 399 (1927).

to form compounds of the general type $\{Me^{(n)}(Ene)_3\}X_n$ in which $Me^{(n)}$ is a n-valent central metallic atom and X a monovalent anion. Cases of this kind follow:

$$\underset{\textit{colorless}}{\{Zn^{II}(Ene)_3\}Cl_2} + 2H_2O;^1 \quad \underset{\textit{pale rose}}{\{Co^{II}(Ene)_3\}(SO_4)};^1$$

$$\underset{\textit{pale violet}}{\{Ni^{II}(Ene)_3\}X_2};^1 \quad \underset{\textit{dark blue}}{\{Cu^{II}(Ene)_3\}X_2};^1$$

$$\underset{\textit{colorless}}{Cd^{II}(Ene)_3\}X_2};^2 \quad \underset{\textit{orange-red}}{\{Co^{III}(Ene)_3\}Br_3} + 3H_2O;^3$$

$$\underset{\textit{orange-yellow}}{\{Cr^{III}(Ene)_3\}Cl_3} + 3H_2O;^4 \quad \underset{\textit{colorless}}{\{Rh^{III}(Ene)_3\}Cl_3} + 3H_2O;^5$$

$$\underset{\textit{colorless}}{\{Ir^{III}(Ene)_3\}I_3};^6 \quad \underset{\textit{colorless}}{\{Pt^{IV}(Ene)_3\}Cl_4} + 2\tfrac{1}{2}H_2O.^7$$

The preparation of such salts differs according to the nature of the central metallic atom. The tri[ethylenediammino] salts of the bivalent metals, such as Zn, Cd, Co^{II}, Ni and Cu, are readily obtained by adding a slight excess of the base to the solution of the salt; the hydroxides precipitated at first will be redissolved if a sufficient quantity of the base is added. The salt of trivalent Co is prepared from the praseo-salt, $\left\{\begin{matrix}Co^{III}(Ene)_2\\Cl_2\end{matrix}\right\}Cl$, which is obtained by oxidizing an aqueous solution of $CoCl_2$ and the base, by means of a current of air from which carbon dioxide has been removed. If the green salt is heated with a third molecule of ethylenediamine on the water bath, the compound desired is secured. The chromium salt is prepared from the corresponding tripyridino compound, $\{Cr^{III}(Pyr)_3Cl_3\}$ by heating it with the base. More volatile bases, such as NH_3 and pyridine, in such complex salts are often expelled from them on heating with less volatile bases

[1] A. Werner and W. Spruck, *Z. anorg. Chem.*, **21**, 229 (1899); F. M. Jaeger, *loc. cit.*, 237.

[2] A. Werner and W. Megerle, *ibid.*, 226.

[3] S. Jörgensen, *J. prakt. Chem.*, (2) **39**, 8 ( ); A. Werner, *Ber.*, **45**, 121 (1912); F. M. Jaeger, *loc. cit.*, p. 182f.

[4] A. Werner, *Ber.*, **45**, 865 (1912); C. Wutke, Dissertation (Zurich, 1918); P. Pfeiffer, *Z. anorg. Chem.*, **24**, 282, 286 (1900); F. M. Jaeger, *loc. cit.*, p. 180f.

[5] A. Werner, *Ber.*, **45**, 1229 (1912); F. M. Jaeger, *loc. cit.*, p. 192.

[6] A. Werner and A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 476, 483 (1920); V. V. Lebedinskiĭ, *Ann. instit. Platine*, **4**, 235 (1926).

[7] A. Werner, *Festschrift, Naturf. Gesell. Zurich*, p. 553 (1917); F. M. Jaeger, *Z. Krist.*, **58**, 172 (1923).

like ethylenediamine; so that this method of preparation, in which such complexes as $\left\{\begin{matrix}Co^{III}(NH_3)_5\\Cl\end{matrix}\right\}Cl_2$ and $\{Cr^{III}(Pyr)_3\}Cl_3$ are chosen to start with, is very often successful if heating is continued for a sufficiently long time. In preparing the rhodium salts one can start with $\{Rh^{III}Cl_6\}Na_3 + 9H_2O$ or dry $RhCl_3$, and heat it with ethylenediamine monohydrate. In the case of the iridium salt it is better to heat $\{Ir^{III}Cl_6\}Na_3 + 12H_2O$ and ethylenediamine with water in sealed tubes at 140°; or to start with sodium dichloro-tetranitro-iridiate

$$\begin{matrix}\{Ir^{III}(NO_2)_4\}\\Cl_2\end{matrix} Na_3 + 2H_2O.$$

Finally, the platinum salt may be obtained from $H_2\{Pt^{IV}Cl_6\}$ by heating it with a strong base in absolute alcohol. Purification can often be accomplished by precipitating the strong cold neutral solution with NaI, since in most cases the iodides of these complex salts are but slightly soluble in water and alcohol. The details are given in the literature cited.

The complex salts of the tri- and tetravalent metals are very stable, even toward acids. The latter do not extract molecules of the base when the solutions are heated with them; nor are the solutions hydrolyzed even at higher temperatures. The salts of the bivalent metals are somewhat less stable, principally toward acids and some, such as the copper salts, sometimes may be appreciably hydrolyzed by water. So far the salts of the tri- and tetravalent metals have been successfully resolved into their optically active antipodes, but this has taken place only rarely in the case of bivalent central atoms since here autoracemization occurs much more easily.

In these cases the method of splitting is chiefly that based upon Pasteur's "second principle", although at present we also know of cases of splitting by spontaneous crystallization, such as that of Pasteur's sodium ammonium racemate below 27°. The principle referred to is that which introduces an optically active compound, or at any rate an optically active radical, into a derivative of the racemoid; afterwards the derivative is easily removed by regenerating

the original substance. If the resulting compounds have sufficiently divergent solubilities they may be obtained separately by repeated fractional crystallization.

For example, let us take the racemoid $\{Co^{III}(Ene)_3\}Cl_3 + 3H_2O$. If a solution of this salt is treated with one molecule of silver *d*-tartrate, COOAg.CHOH.CHOH.COOAg, there is formed a chlorotartrate, $\left\{Co^{III}(Ene)_3\right\}\begin{matrix}Cl\\(d\text{-}C_4O_6H_4)\end{matrix}$. This consists of a mixture of two compounds

$$D\text{-}\left\{Co^{III}(Ene)_3\right\}\begin{matrix}Cl\\(d\text{-}C_4O_6H_4)\end{matrix} \text{ and}$$

$$L\text{-}\left\{Co^{III}(Ene)_3\right\}\begin{matrix}Cl\\(d\text{-}C_4O_6H_4)\end{matrix}$$

which are not each other's mirror images; slow evaporation causes the gradual deposition of beautiful triclinic crystals of $D\text{-}\left\{Co^{III}(Ene)_3\right\}\begin{matrix}Cl\\(d\text{-}C_4O_6H_4)\end{matrix} + 5H_2O$, which is considerably less soluble than the other component.[1] When these crystals have been removed as completely as possible, there remains a solution that does not crystallize at all but finally changes into a gelatinous colloidal mass. If now the solution of the triclinic crystals and a solution of the colloidal mass are treated with NaI, two beautiful crystallized iodides are precipitated, namely, $D\text{-}\{Co^{III}(Ene)_3\}I_3 + H_2O$ and $L\text{-}\{Co^{III}(Ene)_3\}I_3 + H_2O$, whose solutions are strongly active—the first being *dextro*- and the second *levo*-rotary—the specific rotation for each wave-length being the same for both, but having opposite algebraic signs.

The difference in solubility is not always sufficiently great to permit separation by fractional crystallization. In such a case one must try to find another optically active acid or base better suited for the purpose. It has been found, that in addition to *d*- and *l*-tartaric acids, *d*-camphor-sulphonic acid, $HO_3S.C_8H_{13}\begin{matrix}CH_2\\|\\CO\end{matrix}$, and *d*-α-bromo-π-cam-

[1] F. M. Jaeger, *Rec. trav. chim.*, 38, 185f (1919).

phorsulphonic acid, $HO_3S.C_8H_{13}\begin{cases}\text{CHBr}\\ |\\ \text{CO}\end{cases}$, or α-nitrocamphor salts, $C_8H_{14}\begin{cases}\text{CO}\\ |\\ \text{C:NO}_2\end{cases}$. Me^I were useful in this connection. It is a question of ascertaining the best substances by the trial-and-error method; but even then the splitting may often appear to be a very tedious task.

While the Co, Rh, Ir and Pt salts may be separated in this way by means of *d*- or *l*-tartaric acid, the Cr salt is best precipitated by means of sodium *d*-α-nitronate; the *d*-α-camphornitronate of the *levo*-rotary ion is precipitated first, while the salt of the *dextro*-rotary ion remains in solution.[1] The α-nitrocamphor may be eliminated afterwards by precipitation with sodium iodide.

When studying these reactions Werner found, for example, that in the splitting of the Co, Rh, and Cr salts the camphornitronates and chlorotartrates of the *dextro*-rotary complex cobalt ion appeared to be the less soluble, while in the case of the rhodium and chromium salts the salts of the *levo*-rotary ion were less soluble. Making the assumption that the less soluble compounds of the same optically-active acid, obtained from analogously constructed racemoids, would always correspond to the same spatial configuration, Werner concluded from his experiments that if the central cobalt atom was replaced by a chromium or rhodium atom, the rotation of the ion was affected in such a way that its algebraic sign became reversed. This conclusion, however, is erroneous. There is no plausible argument supporting his initial assumption regarding a direct connection between the configuration of the molecules and their relative or absolute solubility. This view is quite arbitrary because, in general, solubility is a so highly complicated and constituent property of matter that, even where we seem to have established rules

[1] A. Werner, *Ber.*, 45, 865 (1912); F. M. Jaeger, *loc. cit.*, p. 201. This method can also be used for the rhodium salt; in both cases the camphornitronates of the *levo*-rotary ions are the less soluble ones and therefore the first precipitated.

for homologous series, sometimes most unexpected and surprising exceptions spring up. This makes these rules quite illusory.

As long ago as 1917, I was able to prove that a much better criterion of analogous or antilogous spatial configurations is based on a comparison of the crystal form, the character of which is extremely sensitive to slight changes in the stereochemical configuration of the atoms because it is a geometrical property. After demonstrating that all optically inactive complex salts of the three metals show a true and very close isomorphism, I was able to prove that the less soluble chloro-*d*-tartrates of the complex cobalt and rhodium salts differed very widely in their crystal forms and even in their degree of hydration. The less soluble chloro-*d*-tartrate of the cobalt salt is triclinic and has five molecules of water, while that of the rhodium salt is monoclinic and contains only four molecules of water. We have here a strong argument for explaining the oppositely directed rotation of their respective complex ions, by the simple fact that they do not have analogous configurations, being on the contrary antilogous.[1] That there is no definitive relation between the spatial configuration of the less soluble compound, in the case of such enantiomorphous isomerides of analogous constitution, has been convincingly demonstrated by Meisenheimer and his fellow workers in their studies on the optically active amine oxides, *e.g.* the optically active antipodes of methylethylnaphthylamine oxide.[2] Recently we have been able to prove conclusively that cobalt and rhodium salts of the same spatial configuration have rotations different in amount, indeed, but identical in sign.[3] In the case where ethylenediamine is replaced by three molecules of the optically active 1,2-cyclopentylenediamine we were able actually to demonstrate that the complex ions of the less soluble chloro-*d*-tartrates of the cobalt and rhodium salts had the same configuration and simultaneously like-directed rotations. We shall consider these arguments again.

[1] F. M. Jaeger, *Chem. Weekblad*, 14, 728 (1917); *Principle of Symmetry*, p. 251ff. (2d ed., 1920); *Rec. trav. chim.*, 38, 196 (1919); A. Werner, *Ber.*, 45, 1229 (1912).

[2] J. Meisenheimer and collab., *Ann.*, 449, 190 (1926).

[3] F. M. Jaeger and H. B. Blumendal, *Z. anorg. Chem.*, 175, 167 (1928).

On comparing the specific rotations of these analogously constituted salts—where all the substitutes about the central metallic atom are the same and similarly arranged—we get an idea of the influence of this central atom on the magnitude of the rotation. The fact that the chromium and cobalt salts are strongly colored and show

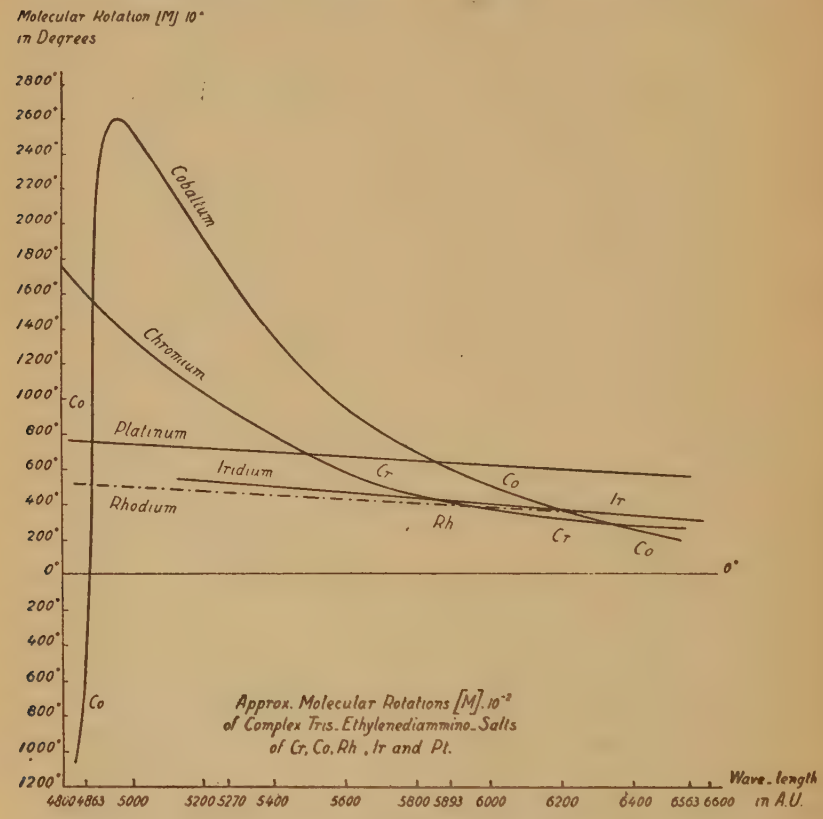


FIG. 23

a very different selective absorption within the visible spectrum, introduces complications. Therefore the colorless rhodium, iridium and platinum compounds are more directly comparable in this respect. One may, however, in in this way obtain a general survey of this influence of the specific nature of the metallic atom. Table I gives the

approximate molecular rotations [M] of the iodides of these salts at four selected wave-lengths.

It appears from Table I that the cobalt salts show the strongest rotation and the maximum rotary dispersion. Next, the chromium salts show, for the smaller wave-lengths, about half the values of the cobalt salts. The rotary dispersion of the platinum, rhodium, and iridium salts, and their rotations, are of the same order of magni-

TABLE I

Approximate Molecular Rotations [M] *of the Iodides of Tri-*[*ethylenediammino*] *complex salts, having the same Spatial Configuration*

(1 gm-mol. per 100 cu. cm.)

Wave-length Å	Chromium salt	Cobalt salt	Rhodium salt	Iridium salt	Platinum salt
6563	+190°	+ 80°	+226°	+226°	+415°
5893	375	630	320	317	505
5270	945	1720	380	420	631
4863	ca.+1600	−1000 ca.	450	—	757
Atom. vol.	7.72	6.76	8.50	8.58	9.08

tude and—for the shorter wave-lengths—appreciably smaller than those of the cobalt and chromium salts (Figure 23). Finally the platinum salt shows a stronger rotation and rotary dispersion than the likewise colorless rhodium and iridium salts; especially for the shorter wave-lengths, however, they are much feebler than those of the cobalt and chromium salts.

For the three colorless salts the degree of rotation increases with the atomic volume; in the case of the cobalt and chromium salts it decreases with increasing atomic volume of the central atom. Organic chemists have often supposed that there must be a chemical contrast between the dissymmetrically arranged substituents, in order to cause strong optical rotation. Evidently this is a mistake, because we found these substituents show no chemical contrast, and nevertheless the observed rotations and rotary dispersions are incomparably greater than they are for organic molecules having four different radicals surround-

ing a carbon atom. Allowing for the influence of the central atom on the magnitude of the rotation, it would appear that the latter is determined chiefly by the special electronic arrangement and distribution within the space surrounding that atom.[1] On the contrary, experience teaches that in several cases we can not demonstrate the development, postulated by Pasteur's law, of hemihedral crystal facets on the enantiomorphous crystals of the antipodes. Thus neither the beautiful tetragonal crystals of *d*- and *l*-tri[ethylenediammino]cobaltic bromide,

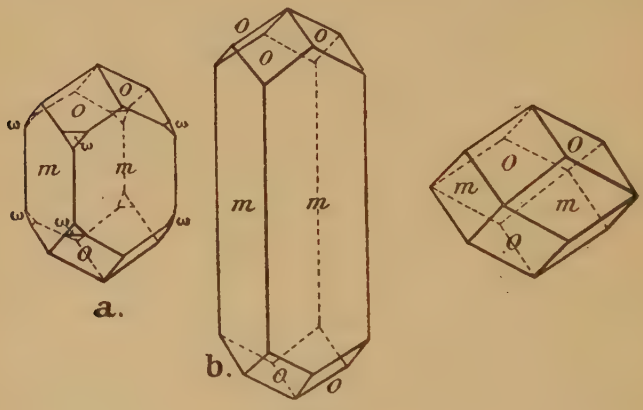


FIG. 24

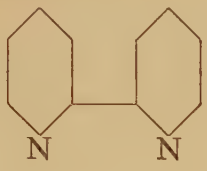
$\{Co(Ene)_3\}Br_3 + 2H_2O$, nor those of the corresponding rhodium salt show any trace of such hemihedral facets,[2] although numerous efforts have been made to obtain them (Figure 24). It may be that in this instance the lack of chemical contrast between substituents exerts some influence, although in many other similar cases—as with the nitrates (Figure 25)—such hemihedrism manifests itself clearly.

On the other hand, it has been found that the special nature of the three equal substituents exerts a great influence upon the magnitude of the rotation, just as does the nature

[1] F. M. Jaeger, "Sur le pouvoir rotatoire des composés chimiques", *Bull. soc. chim.*, (4) 33, 853 (1923); Rapport du 1-ier Conseil de Chimie de l'Instit. Internat. Solvay, p. 160, 169 (Bruxelles, 1922).

[2] F. M. Jaeger, *Rec. trav. chim.*, 38, 190, 198, 209 (1919).

of the central atom. For example, Werner[1] succeeded in separating the complex salt of bivalent Fe and α-α'-dipyridyl, a base of the constitution:



these salts being very stable: $\{Fe^{II}(\alpha\text{-}\alpha'\text{-Dipyr})_3\}X_2$. In the case of the bromide ($+6H_2O$) the splitting was accomplished by means of ammonium *d*-tartrate. The optically active components have a strong tendency to lose

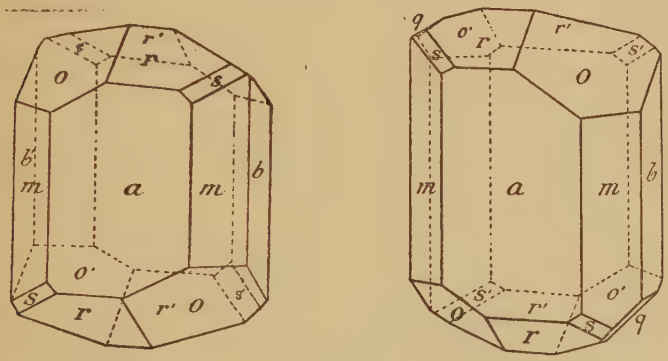


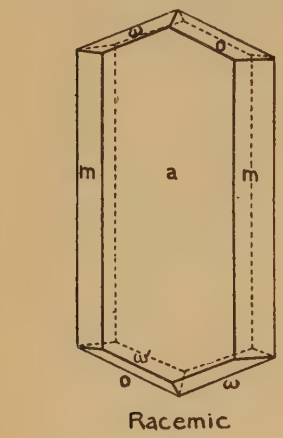
FIG. 25

their activity through autoracemization; their activity was reduced to one-half the original value within a half hour; and the velocity of autoracemization is very great, especially at the beginning. Notwithstanding the fact that the magnitude of rotation must have decreased very considerably at the moment of observation, yet a Nernst lamp revealed a molecular rotation of about 4100°—an angle ten times greater than that for the tri[ethylenediammino] salts. Values of corresponding magnitude were observed in the case of cobalt and rhodium salts of this type with

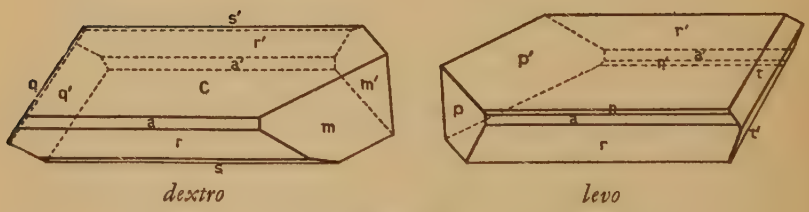
[1] A. Werner, *Ber.*, 45, 433 (1912).

1,2-cyclopentylenediamine.[1] These cases will suffice to illustrate the truth of what has been remarked above.

The corresponding tri[ethylenediammino]-platinic salt was first resolved into its optically active antipodes by Werner, who used *d*-tartaric acid.



Racemic



dextro *levo*

FIG. 26

Racemic salt ($+2\frac{1}{2}H_2O$) *Dextro*-rotary ($3H_2O$) *Levo*-rotary ($3H_2O$)
Tri[ethylenediammino]-platinic chlorides

The racemic chloride is rhombic bisphenoidal; the *dextro*- and *levo*-rotary antipodes are monoclinic sphenoidal and exhibit a clear hemihedrism (Figure 26). The rotary dispersion is normal in this case (see Table I, p. 95.).

[1] F. M. Jaeger and H. B. Blumendal, *loc. cit.* Very high values have also been observed in the case of complex salts of bi- and tri-valent metals with d-oxymethylene-camphor and *l*-aspartic acid, by I. Lifschitz in my laboratory (*Z. physik. Chem.*, 114, 494 (1925).)

CHAPTER VII

Measurement of Optical Rotation

The still more remarkable complex salts of the tri-biacido type will be treated in the same way as the foregoing; but before taking up these, it seems appropriate to interpolate some remarks on the measurement of optical rotation for different wave-lengths. This operation often presents considerable difficulty, because many of this class of salts show a strong selective absorption in the visible portion of the spectrum—a phenomenon not usually met with among carbon compounds.

Most of the measurements were made with a large half-shadow Lippich polarimeter, provided with a monochromator having a symmetrical slit and a carefully calibrated micrometer screw. These instruments, built by Schmidt and Haensch of Berlin, may be had with either a double or a three-fold field of vision. In making these measurements the absorption of the strongly colored salts is often a serious hindrance, making it necessary to use short tubes and very dilute solutions. Fortunately this unfavorable circumstance is often compensated by the very large specific rotation, so that even under these conditions appreciable rotations can be observed.

The specific rotations $[\alpha]$ are calculated by the usual formula: $[\alpha] = \frac{100\alpha}{l.p}$, where α is the observed angle of rotation in degrees, l the length of the tube in decimeters, and p the concentration of the solution (grams per 100 cu.cm.) investigated. The molecular rotation [M] is then $= [\alpha]\frac{M}{100}$, where M is the molecular weight of the salt; [M] is therefore the rotation shown by a solution of one gram-molecule of the substance in 100 cu. cm. of the liquid.

Observations on rotary dispersions, as long ago as 1853, led Biot to conclude that the observed rotation is inversely proportional to the square of the wave-length, λ. Later investigations, however, have shown that the relation between α and λ is generally much more complicated and requires for its expression such a formula as

$$[\alpha] = \frac{A_0}{\lambda^2-\lambda_0^2} + \frac{A_1}{\lambda^2-\lambda_1^2} + \ldots = \Sigma \frac{A_i}{\lambda^2-\lambda_1^2},$$

where A_0, A_1, etc., are characteristic constants and λ_0, λ_1, etc., are wave-lengths characteristic of the different groups of active electrons in the molecule considered.

The simplest case is that in which $[\alpha]$ is determined by a single term only: $[\alpha] = \frac{A_0}{\lambda^2-\lambda_0^2}$; in this case, in which $[\alpha]$ increases regularly with decreasing values of λ over the whole extent of the portion of the spectrum considered, the dispersion curve is a hyperbola and the rotary dispersion is said to be *normal*. If, however, the specific rotation must be expressed by an equation of several terms, *i.e.* if several kinds of active electron groups are co-operating in the molecule, we have to do with a *complex* dispersion. This situation may arise if several kinds of active molecules are present simultaneously in the solution (extramolecular superposition), or if two or more active centra co-operate simultaneously in the same molecule (intramolecular superposition).[1] Complex dispersion is not necessarily abnormal; but, as Biot has already emphasized, it may be abnormal even though both kinds of molecules themselves have normal but different dispersions. For example, even if $[\alpha]$ is expressed by $[\alpha] = \frac{A_0}{\lambda^2-\lambda_0^2} + \frac{A_1}{\lambda^2-\lambda_1^2}$, the rotation may become zero for a wave-length satisfying:

$$\lambda^2 = \frac{\lambda_1^2 A_0 - \lambda_0^2 A_1}{A_0 - A_1} .$$

In this case the dispersion curve can show a maximum or a minimum. The zero value of $[\alpha]$ may, for instance, be

[1] L. Tschugaeff, *Ber.*, 44, 2023 (1911); 45, 2759 (1912).

located within the visible spectrum, if $\lambda_1 < \lambda_0$ but at the same time $A_1 > A_0$. In such cases the dispersion curve is typically abnormal; even "achromatism," or equal rotation for all wave-lengths, may result in such cases.[1]

In the case of the complex salts here considered, the curve of rotary dispersion appears to be abnormal in most cases, when the salts are colored. The abnormal rotation in these cases requires, for its expression, a yet more complicated formula having at least three constants. This abnormality is observed for wave-lengths in the immediate vicinity of some of the absorption bands, provided the absorption bands are really caused by the same radicals in the molecule that cause the optical activity of the latter. Cotton showed in 1896 that this abnormal rotary dispersion is always connected with a "circular dichroïsm," which phenomenon is called the "Cotton effect."[2] It must be remarked once more, that the Cotton effect is not necessarily manifested in the neighborhood of all the absorption bands of the substance investigated, but only near those connected with the optically active groups of electrons in the molecule. Evidently it is important to study the absorption spectra as well as the rotary-dispersion curve of these salts. As for the Cotton effect, this implies that the beam of light emerging from the polarimeter tube is no longer linearly polarized for the special wave-lengths, but is elliptically polarized. Therefore, if precise measurements are to be made, the form of this ellipse must be determined, *i.e.* the dimensions of either axis and the position or angle which the major axis makes with the plane of polarization (or vibration) of the incident beam.

[1] R. Nasini and G. Gennari, *Z. physik. Chem.*, **19**, 117 (1896).

[2] The following references relate to circular dichroïsm and its measurement: A. Cotton, *Ann. chim. phys.*, (7)8,—(1896); M. F. McDowell, *Phys. Rev.*, **20**, 163 (1905); O. D. Tavern, *Ann. phys.*, (4) **32**, 1064 (1910); L. B. Olmstead, *Phys. Rev.*, **35**, 31 (1912); L. Chaumont, *Ann. phys.*, (9) **4**, 61 (1915); N. Lyon, *Ann. Physik*, (4) **46**, 754 (1915); E. Perucca, *Atti accad. sci. Torino*, **54**, 1013 (1919); G. Bruhat, *Ann. phys.*, (9) **3**, 237 (1920); G. Szivessy, *Jahrb. Radioakt. und Elektronik*, **16**, 241 (1921); *Z. Physik*, **6**, 311 (1921); R. de Mallemann, *Compt. rend.*, **175**, 151, 263 (1922). *Theoretical papers:* Carvallo *Compt. rend.*, **122**, 985 (1896); Bates, *Ann. Physik*, **12**, 1080 (1903); E. Darmois, *Ann. chim. phys.*, (8) **22**, 247 (1911); G. H. Livens, *Phil. Mag.*, (6) **25**, 817 (1913); **26**, 362, 535 (1913); **27**, 468, 994 (1914); G. Bruhat, *Compt. rend.*, **153**, 245 (1915); *Bull. soc. chim.*, (4) **17**, 223 (1915); L. Natanson, *J. phys.*, (4) 8, (1909); G. Bruhat, Thèse de doctorat (Paris, 1914).

The direction in which the elliptical orbit is described—clockwise or counterclockwise—must also be determined.

Without going into the mathematical theory of this remarkable phenomenon, its importance for our cases makes it desirable to consider these facts somewhat in detail and give as elementary an explanation as possible of the related questions. In the Appendix (pp. 215ff) the reader will find a brief analytical treatment that will furnish a somewhat more exact statement of the prevailing relationships.

We may start our consideration with Fresnel's well-known explanation of the rotation of the plane of a monochromatic, linearly polarized, beam of light when it passes through an optically-active medium or a column of a solution having the length l.

According to Fresnel's view the incident linearly polarized beam, $s = a \sin n.t$ ($n = 2\pi/T$, if T is the time of vibration of the monochromatic incident light, and a its amplitude), is split into two circularly polarized beams with opposite rotations, but of the same period of vibration, T, as the incident beam when it enters the solution, but only half its amplitude. The characteristic property of such an optically active medium—no selective absorption being present—lies in the fact that these *dextro-* and *levo-*rotary motions are propagated through it at different speeds, v_D and v_L. If l is the thickness of the layer of the medium (length of the column) the two rays consume different times $\tau_1 = l/v_D$ and $\tau_2 = l/v_L$ to traverse the layer, and in consequence of these different retardations they have a certain phase-difference when they are simultaneously reduced to the plane of vibration of the linearly-polarized beam, that is extinguished afterwards by rotating the analyzer through a certain angle. As a result of this difference in phase, the plane of vibration of the emerging beam must be turned through a certain angle α with reference to the original plane if complete extinction is to result. This angle α depends on the phase-difference produced. This phase-difference $= 2\pi/T(\tau_1 - \tau_2)$ in its turn is, of course, proportional to $(\tau_1 - \tau_2)$, *i.e.* also proportional to

the length l of the tube. Fresnel subsequently confirmed experimentally the correctness of his explanation by means of a three-fold quartz prism; later on Cornu and Von Lang confirmed it, using a single quartz prism; and finally Fleischl demonstrated it for solutions also. We shall here accept this view without further discussion.

These relations may be represented by a simple geometrical construction making use of the theorem that two harmonic vibrations of amplitudes *a* and *b* and hav-

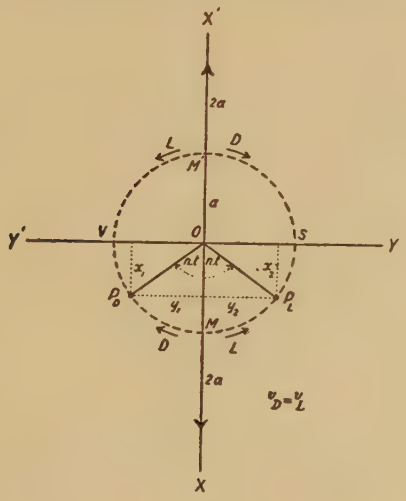


FIG. 27

ing the same period T with phases δ and ϵ respectively, may always be combined into a single harmonic vibration by a construction analogous to the well-known parallelogram of forces (see Appendix page 215). Suppose the linearly polarized beam with the amplitude *a* and vibrating parallel to the axis OX (Figure 27) enters the layer of solution of thickness 1 at the point O in a direction perpendicular to the plane of the figure. All circular motions are supposed to be projected on the same plane. Now if the radius r of the circle equals a/2, then the motions of the oppositely directed circular rays occur along the dotted circle. If the medium is not optically active, the velocities v_D and v_L are equal and the retardation of either ray at

every moment is the same. When the two circular motions simultaneously reach S and V they will be in opposite phases[1] and their resultant along YY′ will be zero. If the two motions meet simultaneously at M, however, their phases are of like sign and the resultant will be a linear vibration parallel with OY and of amplitude $a/2 + a/2 = a$, *i.e.* exactly that of the incident ray. This agrees with the supposition that no absorption takes place during passage through the solution. For intermediate times t, the resultant amplitude is found by the construction mentioned

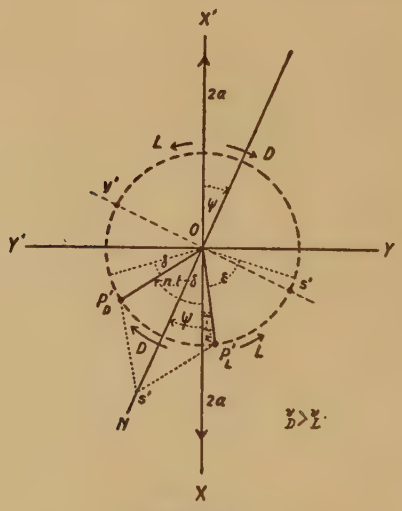


FIG. 28

above. Since the retardations of both rays are assumed to be always equal, the diagonal Os′ (Fig. 28) of the parallelogram P_DOP_Ls' will always have the direction OX, *i.e.* of the plane of vibration of the incident beam. There is no observed deviation in the resulting vibration, just as was to be expected for an optically inactive liquid.

When the nonabsorbing medium is optically active, however, matters are different. In this case v_D and v_L differ

[1] If the original vibration is $s = a \cos n.t$, then its components along OX and OY are: for the *dextro*-rotary one, $x = \frac{1}{2}a.(\cos n.t)$ and $y = \frac{1}{2}a.(\sin n.t)$; for the *levo*-rotary one $x = \frac{1}{2}a.(\cos n.t)$ and $y = -\frac{1}{2}a.(\sin n.t)$. In fact the sum of these components at any instant is always exactly $a \cos n.t$. At S and V, $t = 1/4T, 3/4T, 5/4T$, etc., and $x_D = x_L = O$, $y_D = \frac{1}{2}a$, $y_L = -a/2$; at M and M′ (Fig. 27), however, $t = 0, 1/2T, T$, etc., and $x_D = x_L = a/2$, while $y_D = y_L = 0$.

from each other according to Fresnel's theory. Thus if $v_D > v_L$, then P_D at the moment when the beam has passed through the layer l and is emerging from the tube, has arrived at P_D', while P_L is still at P_L', the phases δ and ϵ of the two rays at that moment being such that the angles $P_D'OX$ and $P'OX'$ (Figure 28) are respectively $(nt-\delta)$ and $(nt-\epsilon)$. Therefore, a resultant amplitude equal to 2a may occur only if P_D and P_L meet simultaneously in the plane ON bisecting the angle $P'OP_D'$, the plane ON making an angle $\psi = l\alpha$, with OX evidently equal to $\frac{1}{2}(\delta-\epsilon)$. Of course the plane of vibration YY' of the analyzer must be turned through this same angle ψ if complete extinction is to be obtained again. Therefore the angle ψ is the observed rotation of the plane of vibration of the incident beam. If S'V' is perpendicular to ON the vibrations in S' and V' will be mutually opposite and their resultant will be zero. Since $\tau_1 = l/v_D$ and $\tau_2 = l/v_L$, the phases of both circular rays are $\delta = \frac{2\pi l}{v_D T}$ and $\epsilon = \frac{2\pi l}{v_L T}$. Therefore in a unit layer of liquid the rotation α will be equal to $\pi/T\,(1/v_D - 1/v_L)$. Therefore the rotation α in this case is negative (quadrant XOY'), if $v_D > v_L$ (*levo*-rotary substance) and positive if $v_D < v_L$ (*dextro*-rotary substance).[1] If the refractive indices of the solution, with respect to a vacuum, are n_D and n_L, respectively, for right- and left-handed circular rays of wave-length λ, then since $n_D = v_0/v_D$, $n_L = v_0/v_L$ and $\lambda = v_0 T$, one may also write $\alpha = \pi/\lambda\,(n_D - n_L)$ for a tube of unit length; or in general $\psi = l\alpha = \pi l/\lambda\,(n_D - n_L)$.

Previous cases are the ordinary ones of an optically-active medium lacking any appreciable selective absorption. If, however, the active group of electrons in the dissolved molecules cause, simultaneously, a strong selective absorption for the wave-length λ, then not only is $v_D \lessgtr v_L$, but the *dextro-* and *levo*-rotary, circularly-polarized vibrations of period T will be unequally absorbed by the liquid. This diminishes the amplitudes of the two emergent rays,

[1] See Appendix page 217. It is in agreement with the usual notation that *levo* rotation ($v_D > v_L$; $n_D < n_L$) corresponds with a negative sign of α, and conversely that a *dextro* rotation occurs clockwise.

to different values p and q. If l is the tube length, C the molar concentration of the solution, and k_D and k_L the molar absorption constants of both rays when traversing a layer of thickness λ, then according to Lambert-Beer's

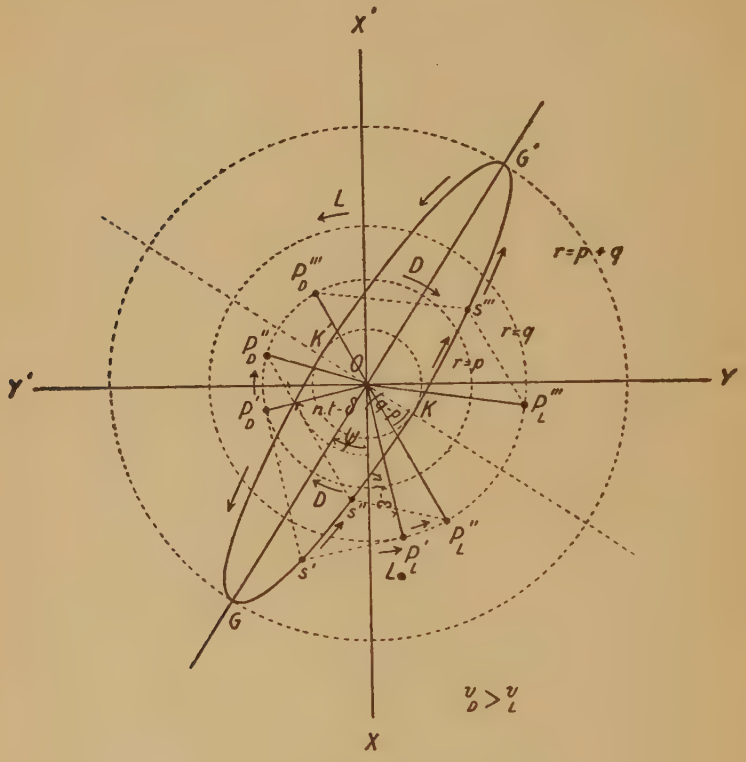


FIG. 29

law we can write $p = \frac{1}{2}\, a.e^{-\frac{2\pi}{2\lambda}.k_D.C.l}$ and $q = \frac{1}{2}\, a.e^{-\frac{2\pi}{2\lambda}.k_L.C.l}$ because the amplitudes are proportional to the square root of the light intensities. Therefore when k_D and k_L differ from each other appreciably (*i.e.* if there is a circular dichroïsm), the amplitudes p and q of both the oppositely-directed, emergent circular rays will also differ noticeably. It is this difference of amplitude of the two circular rays that causes the emergent beam to be not only rotated through ψ, as in the previous case, but also elliptically

instead of linearly polarized. This may be explained by the aid of Figure 29.

The linearly polarized incident beam of amplitude a is here again supposed to be perpendicular to the plane of the figure at O, and all circular and elliptical motions are again projected on this plane. The vibrations of the incident beam are parallel to OX. The motion of both the oppositely-directed circular rays may now be represented as taking place on the dotted circles of the radii q and p ($q > p$). According to the different speeds v_D and v_L and the resultant difference in their phases δ and ϵ, a rotation ψ will be observed, just as in the preceding case, the angle again being $\frac{1}{2}(\delta - \epsilon)$. In the direction ON the resultant amplitude will be $(q + p)$. At the points S′ and V′, however — S′V′ being perpendicular to ON — the phases will be opposite and the amplitudes are different, so that the resultant amplitude is no longer zero, but has the value $(q - p)$. It can be mathematically demonstrated (see the Appendix) that the complete motion of the emerging ray occurs over an elliptical orbit whose principal axes are $(q + p)$ and $(q - p)$, the major axis being rotated through an angle ψ with respect to the original plane of vibration OX.

The ellipticity of the orbit is measured by $(q - p) \div (q + p) = \tan \beta$. As this ellipticity is usually a very small quantity, we may often take β itself in place of $\tan \beta$. From the above values for p and q it follows that in this case β (= ellipticity) $= \pi(k_D - k_L).C.l/\lambda$.[1]

In the case here considered k_D was supposed to be greater than k_L, so that $q > p$; the elliptic orbit therefore is traversed in a counterclockwise direction although v_D, being greater than v_L, makes the rotation ψ negative (*levo*-rotation). Evidently there are four distinct cases here discernable:

[1] As a matter of fact

$$\tan \beta = \frac{e^{-\frac{\pi k_D.C.l}{\lambda}} - e^{-\frac{\pi k_L.C.l}{\lambda}}}{e^{-\frac{\pi k_D.C.l}{\lambda}} + e^{-\frac{\pi k_L.C.l}{\lambda}}} = \frac{1 - e^{-\frac{\pi(k_L - k_D)C.l}{\lambda}}}{1 + e^{-\frac{\pi(k_L - k_D)C.l}{\lambda}}}$$

which for small values of β gives the expression above, if terms of the third and higher orders be neglected.

(1) $v_D > v_L$ and $k_D > k_L$; then $q > p$; rotation negative; substance *levo*-rotary; elliptical orbit traversed counter-clockwise; minor axis = $(q - p)$.

(2) $v_D > v_L$ and $k_D < k_L$; then $q < p$; rotation negative; substance *levo*-rotary; elliptical orbit traversed clockwise; minor axis = $(p - q)$.

(3) $v_D < v_L$ and $k_D > k_L$; then $q > p$; rotation positive; substance *dextro*-rotary; elliptical orbit traversed counter-clockwise; minor axis = $(q - p)$.

(4) $v_D < v_L$ and $k_D < k_L$; then $q < p$; rotation positive; substance *dextro*-rotary; elliptical orbit traversed clockwise; minor axis = $(p - q)$.

These four cases are represented diagramatically in Figure 30.

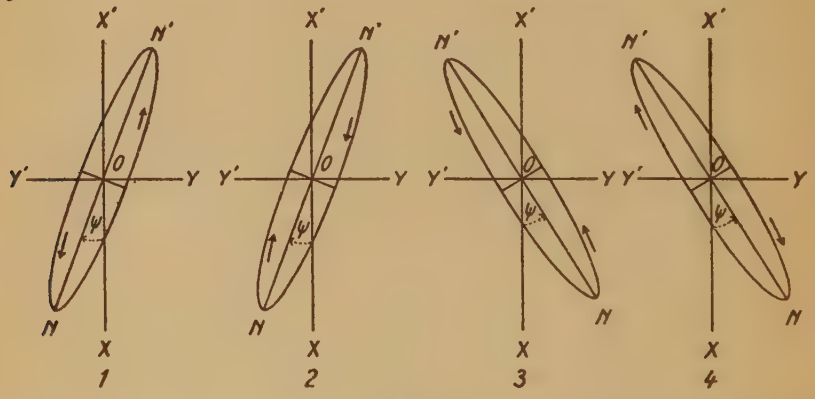


FIG. 30

The rotation always takes place in the direction of that circular ray whose velocity is smaller in the given medium. The elliptic orbit is traversed in that direction characteristic of that circular ray which is least absorbed during its passage through the medium (solution).[1]

Modern measurements of the Cotton effect in optically active absorbing solutions—*e.g.* those by Bruhat—have made it evident that the ellipticity of the emergent beam is negligible for wave-lengths far removed from those of the

[1] A general discussion of anomalous rotary dispersion will be found in H. Grossmann and M. Wreschner, *Die anomale Rotationsdispersion* (Samml. chem. techn. Vorträge, Bd. 26, Stuttgart, 1921).

absorption band; that it increases as the band is approached and reaches a maximum at about the center of the band. The abnormal rotation attains a maximum on entering the absorption band; then diminishes very rapidly, becoming zero at the middle of the band; and increases to another maximum, but with opposite sign, at the other boundary of the band (See Fig. 79, p. 227). We shall meet an example of this when we consider the complex trioxalates of the trivalent metals.

Circular dichroïsm often occurs in the case of these colored complex salts, and to completely determine its character it is necessary first to measure the angle ψ in the usual way, *e.g.* by means of a Lippich's prism. If the ellipticity and the rotation are both small, this can be done without difficulty. In all other cases it is necessary to measure the angle β (see Appendix, Figs. 76, 77, 81) because tan β gives directly the ratio of the major and minor axes of the elliptic orbit, *i.e.* the value of $(q-p)/(q+p)$. If now we take the angle β itself instead of tan β, it follows from the preceding that the ellipticity is given by the expression $\beta = \frac{\pi(k_D - k_L)C.l}{\lambda}$. In this way the part played by the differing mode of absorption of the two rays is allowed for and we obtain a measure of the circular dichroïsm.

Later on we shall see that this different degree of absorption of *dextro-* and *levo-*rotary vibrations by a colored optically-active medium, is also a fact of great importance in the possible solution of the problem of the so-called "total asymmetrical synthesis" by photochemical processes.

Measurement of the angle β must be made with the aid of a so-called "elliptic analyzer," the principal portion of which is a compensator, *i.e.* an optical device for re-establishing a linearly polarized from the elliptically polarized beam. Methods of this kind were developed by Babinet (compensator adjusted for $1/4\lambda$), by Bravais, Fresnel, Brace, Zakrzewski, Perucca,[1] and many others.

[1] E. Perucca, *Atti accad. sci. Torino*, 54, 1013 (1919); *Nuovo cimento*, (6) 5, 1 (1913); M. C. Zakrzewski, *Bull. acad. sci. Cracovie*, 1016 (1907).

We ourselves ordinarily use a quarter-wave-length mica plate for this purpose, in combination with a so-called Bravais-double-plate[1] as an indicator for determining when the elliptic vibration has actually become a completely linear one. When this condition is reached, the two halves of the Bravais-plate have equal illumination (see Appendix). Since we can not have such quarter-wave-length plates (achromatic compensators) for every wave-length, we use four such plates prepared for mean red, green, blue, and violet, and apply the necessary corrections as determined by Perucca's method.[2] Although somewhat troublesome, this method yields very good results even in those cases where the considerable ellipticity makes it impossible to measure the rotation ψ directly. In the latter case the value of ψ must be deduced from supplemental measurements. In such cases the optical rotation of the liquid can not be simply determined by means of an ordinary polarimeter (for the details of these methods see the Appendix, p. 228).

[1] Such a plate is a crystal (mica) plate of about a quarter-wave-length thickness, halved in such a way that the cut makes an angle of 45° with the principal optical directions. The upper half is then turned through 180° about an axis perpendicular to the plane of the section (upside down) and is then cemented to the other half along the line of intersection. By this arrangement the line of section makes, in either half, an angle of 45° with the corresponding equivalent optical directions (see Appendix).

[2] Perucca, *loc. cit.*; Zakrzewski, *loc. cit.*

CHAPTER VIII

Complex Salts of Tri-biacido Type.

The phenomena shown by the complex salts of the tri-biacido type mentioned above, present to us in a remarkable manner the properties just considered and I proceed to take up the phenomena they show. These salts form a sub-group of the hexacido salts, the dibasic acids such as oxalic, malonic and the like, or hydroxy acids such as salicylic and some diphenols, or such analogous compounds as pyrocatechol and alizarin, occupying two coördinate positions in these complex ions. Inorganic acids, such as sulphuric and sulphurous, also form complex salts of this type but most of them have not yet been studied with reference to their possible splitting into optical antipodes.

The salts best studied, in this respect, are the trioxalato salts although even here much remains to be done. These salts are known for the bi-, tri-, and tetravalent metallic atoms; but we shall be chiefly occupied with those of the trivalent metals, because so far these have proved to be best suited for resolution into optically-active isomerides.

Some instances of such complex oxalates are given below:

$\{Co^{II}(C_2O_4)_3\}(NH_4)_4 + 6H_2O$, rose colored;[1]
$\{Co^{III}(C_2O_4)_3\}K_3 + 3H_2O$, dark black-green;[2]
$\{Cr^{III}(C_2O_4)_3\}K_3 + 3H_2O$, purplish-blue;[3]
$\{Fe^{III}(C_2O_4)_3\}K_3 + 3H_2O$, emerald-green;[4]
$\{Mn^{III}(C_2O_4)_3\}K_3 + 3H_2O$, green;[5]

[1] F. Ephraïm, *Ber.*, **42**, 3850 (1909).
[2] S. P. L. Sörensen, *Z. anorg. Chem.*, **11**, 5 (1896); F. M. Jaeger, *Rec. trav. chim.*, 38, 247 (1919).
[3] H. Croft, *Jahresb. Pharm.*, **23**, 235 (1840); A. Werner, *Ber.*, **45**, 3061 (1921); F. M. Jaeger, *Rec. trav. chim.*, 38, 243 (1919).
[4] F. Beilstein, *Handbuch d. organischen Chemie*, vol. II, p. 527 (4th ed., 1920); F. M. Jaeger, *loc. cit.*, p. 242; W. Thomas and E. Rideal, *J. Chem. Soc.*, **121**, 196 (1922); **119**, 1140 (1921).
[5] R. Wagner, *Ber.*, **22**, 288 (1889). Review.

$\{V^{III}(C_2O_4)_3\}K_3 + 3H_2O$, green;[6]
$\{Rh^{III}(C_2O_4)_3\}K_3 + 4\frac{1}{2}\ H_2O$, blood-red;[7]
$\{Ir^{III}(C_2O_4)_3\}K_3 + 4H_2O$, yellow;[8]
$\{Ru^{III}(C_2O_4)_3\}K_3 + 4\frac{1}{2}\ H_2O$, brown;[9]
$\{Al^{III}(C_2O_4)_3\}K_3 + 2\frac{1}{2}$ *or* $3H_2O$, colorless;[10]
$\{Sb^{III}(C_2O_4)_3\}K_3 + 3, 4, 8$ *or* $12H_2O$, colorless;[11]
$\{Bi^{III}(C_2O_4)_3\}(NH_4)_3 + 5H_2O$, colorless;[12]
$\{Y^{III}(C_2O_4)_3\}K_3 + 9H_2O$, colorless;[12a]
$\{Sn^{IV}(C_2O_4)_3\}K_2 + \frac{1}{2}K_2C_2O_4 + 2\frac{1}{2}H_2O$, colorless.[13]

In the same way malonic acid gives:

$\{Fe^{III}(C_3O_4H_2)_3\}K_3 + 4H_2O$, green;[14]
$\{Cr^{III}(C_3O_4H_2)_3\}K_3 + 3H_2O$, purplish-blue;[15]
$\{Rh^{III}(C_3O_4H_2)_3\}K_3 + 3H_2O$, orange;[16]
$\{Mn^{III}(C_3O_4H_2)\}_3K_3$, red;[17]

and salicylic acid gives:

$\{Fe^{III}(C_7O_3H_4)_3\}K_3 + 1\frac{1}{2}H_2O$, orange-red;[18]
$\{Ti^{IV}(C_7O_3H_4)_3\}Na_2$, gold-yellow.[19]

Pyrocatechol gives:

$\{Fe^{III}(C_6H_4O_2)_3\}K_3 + 2H_2O$, dark brown;[20]
$\{Cr^{III}(C_6H_4O_2)_3\}K_3$, green;[21]
$\{Si^{IV}(C_6H_4O_2)_3\}(NH_4)_2$, colorless;[19]
$\{Al^{III}(C_6H_4O_2)_3\}K_3 + 1\frac{1}{2}H_2O$, colorless;[22]

[6] A. Piccini and N. Brizzi, *Z. anorg. Chem.*, 19, 402 (1889); A. Bultemann, *Z. Elektrochem.*, 10, 141 (1904).
[7] E. Leidié, *Ann. chim. phys.*, (6) 17, 307 (1889); H. Dufet, *Bull. soc. minér.*, 12, 466 (1889); A. Werner, *Ber.*, 47, 1954 (1914); F. M. Jaeger, *loc. cit.*, 256.
[8] C. Gialdini, *Gazz. chim. ital.*, 38,ii, 492 (1908); M. Délépine, *Compt. rend.*, 159, 239 (1914); *Bull. soc. chim.*, (4) 21, 161 (1917); F. M. Jaeger, *loc. cit.*, 270.
[9] R. Charonnat, *Compt. rend.*, 178, 1279, 1423 (1924).
[10] A. Rosenheim and L. Cohn, *Z. anorg. Chem.*, 11, 182 (1896); F. Kehrmann and N. Pickersgill, *ibidem*, 4, 134 (1893).
[11] N. Svenssen, *Ber.*, 3, 314 (1870); A. Rosenheim, *Z. anorg. Chem.*, 20, 290 (1899); R. Wagner, *loc. cit.*; A. Souchay and E. Lenssen, *Ann.*, 105, 255 (1858).
[12] A. Rosenheim, *Z. anorg. Chem.*, 20, 305 (1899).
[12a] R. J. Meyer *in* Abegg, *Handbuch der Anorganischen Chemie*, v. III-i, p. 332 (Leipzig, 1906).
[13] R. E. Weinland and H. Kuhl, *Z. anorg. Chem.*, 54, 244, 253 (1907).
[14] H. Scholz, *Monatsh.*, 29, 439, 443, 445 (1908); F. M. Jaeger, *loc. cit.*, 285.
[15] W. Lapraik, *J. prakt. Chem.*, (2) 47, 321 (1893); F. M. Jaeger, *loc. cit.*, 294.
[16] F. M. Jaeger, *Rec. trav. chim.*, 38, 300 (1919).
[17] J. Meyer and W. Schramm, *Z. anorg. Chem.*, 123, 62 (1922).
[18] R. F. Weinland and A. Herz, *Ann.*, 400, 219 (1913).
[19] A. Rosenheim and O. Sorge, *Ber.*, 53, 932, 938 (1920).
[20] R. F. Weinland and K. Binder, *Ber.*, 45, 148, 1113 (1912).
[21] R. F. Weinland and E. Walter, *Z. anorg. Chem.*, 126, 141 (1923).
[22] R. F. Weinland and W. Denzel, *Ber.*, 47, 737 (1914).

$\{Mn^{III}(C_6H_4O_2)_3\}(NH_4)_2 + 5H_2O$, dark green;[1]

$\{As^{V}(C_6H_4O_2)_3\}H + 5H_2O$, colorless.[2]

Alizarin gives:

$\{Fe^{III}[C_6H_4.(CO)_2.C_6H_2O_2]_3\}K_3 + 8H_2O$, dark black-red.[3]

Among the trisulphates of this type we may mention $\{Ir^{III}(SO_4)_3\}K_3 + H_2O$[4] and $\{Fe^{III}(SO_4)_3\}Na_3 + 3H_2O$ (Ferronatrite);[5] for a discussion of the trisulphites of trivalent cobalt, rhodium, and iridium, see the literature mentioned below.[6]

The special methods of splitting the complex trioxalates and trimalonates are based on the same Pasteur principles as those used with the tri[ethylenediammino] salts, viz., the combination with an easily removable optically-active substance. Since the complex ions are anions in this case, carrying a triple negative electric charge, the metal atoms to which they are linked must here be replaced by optically-active bases. For this purpose we may use strychnine, $C_{21}H_{22}N_2O_2$, as in the case of trioxalato-cobaltiate, chromiate, rhodiate and iridiate,[7] and of trimalonato-chromiate;[8] or cinchonine, $C_{19}H_{22}N_2O$, as in the case of potassium trimalonato-rhodiate.[9] In the case of potassium trioxalato-ferriate the splitting was obtained by means of *d*- and *l*-α-phenylethylamine, $C_6H_5.CH(CH_3).NH_2$. Sometimes it is not advisable to use the tristrychnine salts but rather the alkali-distrychnine or the hydrogen-distrychnine salts, for example, in the case of the chromium salts of both series.[10] In the single case of potassium trioxalato-cobaltiate it has

[1] R. F. Weinland and H. Sperl, *Einführung in die Chemie der Komplexverbindungen*, p. 149 (Stuttgart, 1924).

[2] A. Rosenheim and W. Plato, *Ber.*, 58, 2000 (1925); R. F. Weinland and J. Heinzler, *ibidem*, 52, 1322 (1919).

[3] R. F. Weinland and K. Binder, *Ber.*, 47, 977 (1914).

[4] M. Délépine, *Compt. rend.*, 142, 1525 (1906); Lecocq de Boisbaudran, *ibidem*, 96, 1406 (1883).

[5] R. F. Weinland and F. Ensgraber, *Z. anorg. Chem.*, 84, 349 (1913).

[6] E. Berglund, *Ber.*, 7, 469 (1874); K. Seubert and K. Kobbe, *ibid.*, 23, 2558 (1890); C. Birnbaum, *Ann.*, 136, 183 (1865); C. Claus, *Ann.*, 63, 352 (1847).

[7] F. M. Jaeger, *Rec. trav. Chim.*, 38, 245, 251, 263 265, (1919). One can often use successfully brucine, morphine, and even yohimbine for such splitting.

[8] *Idem*, p. 296.

[9] *Idem*, p. 305.

[10] A. Werner, *Ber.*, 45, 3061 (1912); F. M. Jaeger, *loc. cit.*, 245, 297.

been found that a splitting by spontaneous crystallization[1] (Pasteur's first method) took place if the temperature of crystallization exceeded 13.2°—a maximum transition temperature for the racemoid. I shall return to the relation here considered, later on.

In the case of these complex salts the possibility of obtaining the optically-active antipodes in the free state is often seriouly impeded by their rapid autoracemization while the antipodes of the rhodium and iridium salts, for instance, appear to be very stable and show no appreciable autoracemization in solution even at higher temperatures. The salts of chromium, cobalt, iron and rubidium are, in decreasing order, much less stable; so that in the case of iron, for example, only a very rapid transient activity could be determined,[2] or no fission at all took place.[3] This fact is due to the frequent secondary ionization of these ions in solution, thus:

$$\{Fe(C_2O_4)_3\}''' \rightleftarrows \{Fe(C_2O_4)_2\}' + C_2O_4''$$

$$\{Co(C_2O_4)_3\}''' \rightleftarrows \{Co(C_2O_4)_2\}' + C_2O_4''$$

On re-entering the monovalent complex ion thus formed the detached C_2O_4'' ion can take the one position or the other, after slightly shifting one of the C_2O_4'' ions still present within the complex ion, thus producing either the *dextro-* or the *levo*-rotary ion and with equal chances. In some cases, such as that of the chromium salts, the hydrolyzing influence of the water in the solution also often makes itself felt by causing H_2O molecules or HO groups to enter the anion. In such cases as these, the rôle of the intermediate detachment of one or more of the radicals about the central metallic ion is very evident in the process of autoracemization. The peculiar instability of the ion in the trioxalato-cobaltiate ion is further illustrated by its

[1] F. M. Jaeger and W. Thomas, *Rec. trav. Chim.*, 38, 249 f (1919).

[2] W. Thomas, *J. Chem. Soc.*, 119, 1140 (1921). At room temperature the rotary power of the trioxalate was reduced to one-half of its original value within 15 minutes. R. Charronnat, *Compt. rend.*, 178, 1279 (1924).

[3] F. M. Jaeger, *op. cit.*, p. 293; the potassium trimalonato-ferriate could not be separated into its antipodes by means of either strychnine, brucine, or cinchonine.

high sensitivity to light radiation, the latter strongly accelerating its decomposition according to the reaction:[1]

$$2\{Co(C_2O_4)_3\}''' = 2\{Co^{II}(C_2O_4)_2\} + C_2O_4'' + 2CO_2$$

and

$$2\{Co(C_2O_4)_2\}'' = 2CoC_2O_4 + 2C_2O_4''$$

the three C_2O_4'' ions being eliminated from the solution as $3K_2C_2O_4$ by the $K^{\cdot}$ ions of the original salt simultaneously present in the solution.

In the case of $\{Fe^{III}(C_2O_4)_3\}'''$ light radiation causes this ion to produce: $2\{Fe^{II}(C_2O_4)\}'' + C_2O_4'' + 2CO_2$ in an analogous manner.

The splitting of potassium trioxalato-ferriate was accomplished by means of the optically active α-phenylethylamines, the *l*-base giving the *levo*-rotary complex ion as the least soluble salt and the *d*-base that of the *dextro*-rotary ion. Since the rotation dropped to half its original value within fifteen minutes, and since the velocity of autoracemization, as a function of time, is known, the true rotation for sodium light had to be extrapolated, $[\alpha]_D$ being 356° and $[M]_D$ about 1748°. In the case of this splitting, with *l*-α-phenylethylamine the *levo*-rotary salt only was obtained and no trace found of the other component. In fact there sets in an equilibrium between the *l*-complex-*l*-base and *d*-complex-*l*-base; and as the first salt is the less soluble it is deposited continuously, so that there is the following shift in equilibrium:

d-complex-*l*-base $\rightarrow$ *l*-complex-*l*-base,

and finally nothing of the first salt remains.

Up to the present the rather unstable trimalonato-ferric salt $\{Fe^{III}(C_3O_4H_2)_3\}K_3 + 4H_2O$ has not been split into its antipodes.

A similar, but more complicated case, is found in the splitting of potassium trioxalato-chromiate by means of strychnine.[2] The compound here used was the potassium di-strychnine salt ($+ 4H_2O$) and the remarkable fact was found that, in a solution containing alcohol, the splitting gave only the salt of the *dextro*-rotary complex ion; while

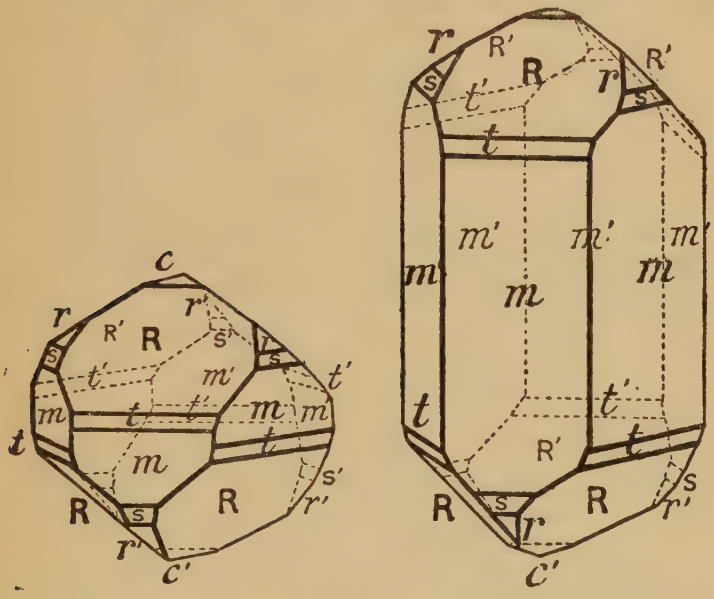
[1] F. M. Jaeger and G. Berger, *Rec. trav. chim.*, 40, 153 (1921).
[2] A. Werner, *Ber.*, 45, 3061 (1912).

in an aqueous solution alone the *levo*-rotary salt was obtained after removing the strychnine from the resulting crystallization product. On analyzing these crystals, precipitated from the alcoholic solution by concentration on the water bath, it was found that these less soluble crystals were composed of the potassium distrychnine salt ($+ 4H_2O$) of the *dextro*-gyrate ion. The explanation must be that in solution, and especially at higher temperatures, there occurs a very rapid racemization. Since the potassium distrychnine salt of the *dextro*-rotary ion is sparingly soluble in alcohol it is precipitated first—thereby disturbing the equilibrium and therefore is immediately regenerated from the other component. Continued concentration of the solution causes its subsequent gradual deposition until the other component is exhausted, it having been completely transformed by racemization into the less soluble component. In the second case, however, where an aqueous solution is used, the tristrychnine salt is formed by the action of the solvent upon the potassium distrychnine salt, and as the tristrychnine derivative of the *levo*-rotary ion is much less soluble in water than the other component, that salt is precipitated first as the solution is concentrated. This precipitation causes a displacement of the equilibrium under the influence of the autoracemization, and a fresh amount of the salt of the *levo*-rotary ion is produced every time. Such phenomena have been observed in the past, for instance, by Pope and Peachy. The remarkable fact in such cases is that a complete inversion of one antipode into the other is effected solely by a simple process of crystallization, the active form being produced from the racemoid only during recrystallization.

While the racemic bluish violet potassium trioxalatochromiate $\{Cr^{III}(C_2O_4)_3\}K_3 + 3H_2O$ crystallizes in the monoclinic-prismatic class[1] and therefore possesses a symmetry plane, it has not yet been possible to obtain the optically active antipodes ($+ 1H_2O$) in a measurable form. They are probably trigonal, like the other active salts of cobalt, rhodium, and the like. Their optical rotation is

[1] F. M. Jaeger, *Rec. trav. chim.*, 38, 244, 246 (1919). The racemic salt is isomorphous with the corresponding ferric salt, but not with the cobaltic salt which contains $3\frac{1}{2}$ molecules of H_2O and is triclinic-pinacoidal.

strongly abnormal and the enormous rotary dispersion causes the fields of the polarimeter prism to be colored in strikingly different hues—a phenomenon often observed in such cases as a consequence of the strong circular dichroïsm accompanying the abnormal rotary dispersion. The rapid autoracemization in solution makes it possible to deter-



Dextro *Levo*

FIG. 31

Potassium trioxalato-cobaltiates

mine the corresponding curve only approximately for a water-acetone solution; the values obtained give a curve quite analogous to that for the corresponding cobaltic salt (Fig. 36), the maxima and minima are here shifted to other wave lengths, however, because of the wholly different location of the absorption bands of the solution.

The racemic and optically active cobalt salts[1] have been studied in just the same way.

The dark green racemic salt ($+ 3\frac{1}{2}H_2O$) is triclinic-pinacoidal, but is not isomorphous with the corresponding

[1] *Ibidem*, 247, 253.

racemoids of the rhodium and iridium complexes, which contain $4\frac{1}{2}$ molecules of water. The optically active antipodes are trigonal-trapezohedral and much resemble the crystals of *dextro-* and *levo-*rotary quartz, as do the crystals of the corresponding rhodium salts. The hemihedrism of the optically active rhodium salts is easily observed by the occurrence of the facets of the trigonal bipyramids—{2241} for the right- and {42$\bar{2}$1} for the left-hand crystals; in the case of the optically active cobaltic salts such hemihedral development has been very rarely observed (Figure 31). This latter circumstance has somewhat delayed the discovery of the spontaneous splitting of the cobaltic salts, because it was impossible to sort out the left- and right-handed crystals from the solution. However, the occurrence of its spontaneous splitting above 13.2° was demonstrated by determining the rotation of the crystals separately; when collected at random from the solution they may be either *dextro-* or *levo-*gyrate.

By determining the solubility of the racemoid and of the optically active components throughout a considerable range of temperature, it was possible to fix the transition temperature of the racemoid at 13.2° under one atmosphere —the optically active salts representing the stabler phases with respect to the racemic compound at all temperatures above that point. This temperature is, therefore, a maximum transition temperature for the racemoid. The reaction there taking place is:

$$2[K_3\{Co(C_2O_4)_3\} + 3\tfrac{1}{2}H_2O] \overset{13.2^\circ}{\rightleftarrows} [d\text{-}K_3\{Co(C_2O_4)_3\} + 1H_2O] + [l\text{-}K_3\{Co(C_2O_4)_3\} + 1H_2O] + 5H_2O.$$

According to the theorem of "mobile equilibrium" (Braun-Le Chatelier-van't Hoff) the splitting of the racemoid into the optically active components and 5 H_2O is an endothermic process, which therefore requires a supply of heat from without. Below 13.2° the racemoid has a lower solubility than the antipodes, above 13.2° the antipodes are the less soluble (Figure 32).[1]

Later on we shall meet with other cases of spontaneous splitting of complex salts; but the case here considered was

[1] F. M. Jaeger, *loc. cit.*, p. 250.

the first one to be discovered—Werner's apparent similar results with trioxalato-rhodiates were later proved to be erroneous.[1] The general relations of these salts are of the highest importance for the understanding of the mutual behavior of racemoids and antipodes, I shall therefore consider them in more detail later on. At present we will continue the discussion of the optical behavior of the active cobaltic salts.

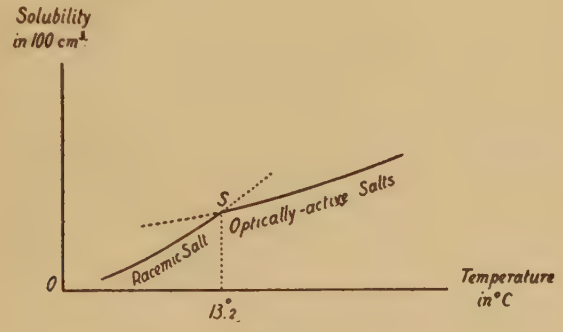


FIG. 32

When strychnine sulphate is added to the solution of the racemic compound, there is precipitated first the least soluble strychnine salt of the *levo*-rotary ion.[2] In all these cases the strychnine is easily replaced by potassium, by precipitating the organic base with potassium iodide and repeatedly recrystallizing the product after the strychnine iodide has been filtered off.

The specific rotations [α] observed for the chromic and the cobaltic salts are given in Table II.

The cobaltic salt also shows a strongly abnormal rotary dispersion and a Cotton effect in the neighborhood of the absorption band. A 0.41-per-cent solution absorbs very strongly all rays between 5515 Å and 6520 Å; a 0.27-per-cent solution absorbs all wave-lengths between 5750 Å and 6450 Å.

[1] A. Werner, *Ber.*, 47, 1954 (1914); F. M. Jaeger, *Proc. Acad. Sci. Amsterdam*, 20, 264f. (1917); *Rec. trav. chim*, 38, 269 (1919).

[2] In the case of the rhodium and iridium compounds this is the salt of the *dextro*-rotary ion; but, as has been pointed out, this does not prove the antilogous configuration of these ions with respect to that of the cobalt salt.

TABLE II.

Specific Rotations of the Levo *Salts of Chromium and Cobalt.*

Wave-length A	Specific Rotation [α] *l*-Cr-salt*	*l*-Co-salt
4740	− 486°	− 65.5°
4780	− 505	− 87.9
4870	− 543	− 91.5
4945	—	− 96.6
5020	—	− 101.8
5105	—	− 107.6
5180	− 675	− 111.9
5260	—	− 120.8
5340	− 655	− 130.4
5420	− 620	− 140.1
5515	− 410	− 154.3
5610	− 265	− 172.0
5700	0	− 190.2
5800	+ 515	− 213.0
5910	+ 575	− 248.3
6020	—	− 277.0
6140	+ 185	− 183.5
6260	—	+ 4.0
6340	0	—
6380	− 25	+ 118.9
6520	− 66	+ 92.3
6660	—	+ 38.0
6800	—	+ 7.5
6940	—	+ 4.2

* The observed values are about one-third lower; but allowance for the velocity of racemization in water and acetone gives the values as here printed.

The corresponding racemic rhodium salt[1] was

$$\{Rh^{III}(C_2O_4)_3\}K_3 + 4\tfrac{1}{2}H_2O,$$

obtained by Leidié's method[2] in large fine crystals (Fig. 33) of triclinic pinacoidal symmetry, that are not isomorphous with those of the corresponding cobaltic salt but with the iridium salt which also contains 4.5 molecules of water.[3]

[1] A. Werner, *Ber.*, 47, 1954 (1914); F. M. Jaeger, *loc. cit.*, p. 256, 259-70.
[2] Leidié, *loc. cit.*
[3] A. Werner and F. M. Jaeger, *op. cit.*, pp. 270, 274-284.

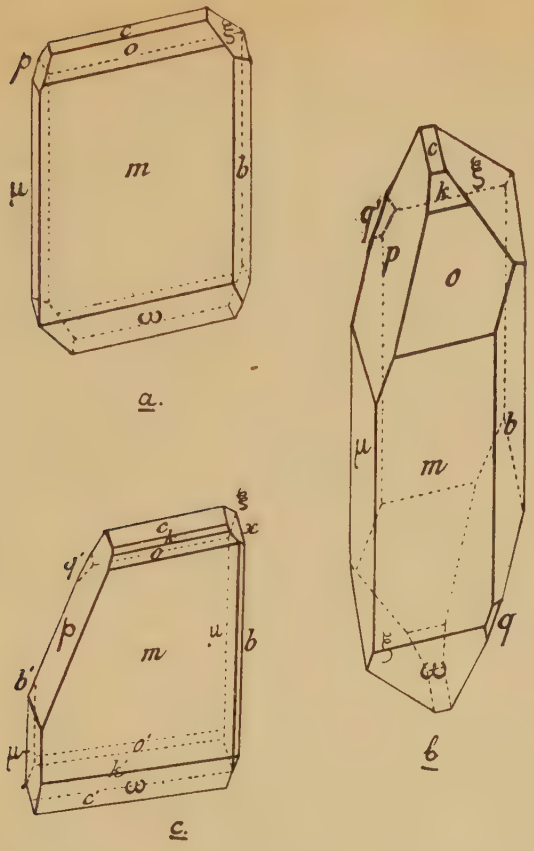


FIG. 33
Racemic Potassium trioxalato-rhodiate ($+4\frac{1}{2}H_2O$)

The crystals of the rhodium salt show a rather variable and often apparently asymmetric habit—a fact that lead Werner to the erroneous view that they were crystals of the antipodes. In both cases the optically active salts are of trigonal-trapezohedral symmetry, those of the rhodium salts having the appearance of quartz crystals (Figure 34),[1] while those of the iridium salts have the shape of trigonal bipyramids (Figure 35).[2] Their angular values also differ

[1] A. Werner and F. M. Jaeger, *op. cit.*
[2] F. M. Jaeger, *loc. cit.*, pp. 270, 274–284.

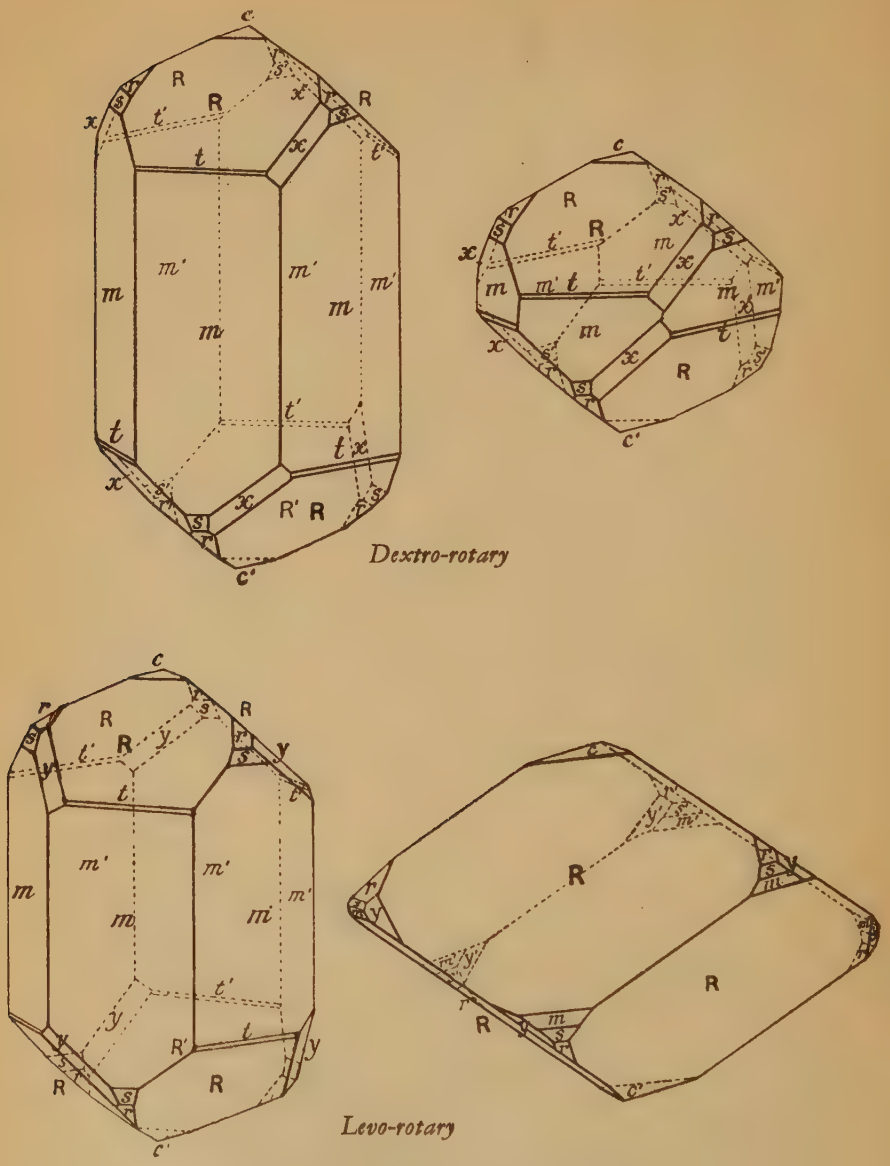


FIG. 34. *Dextro-* and *levo*-rotary
Potassium trioxalato-rhodiates ($+1H_2O$)

from those of the rhodium salts to a more appreciable extent than is commonly observed in the case of isomorphous substances.

Pasteur's principle respecting the enantiomorphous crystal form of the antipodes evidently holds good in this case. In the case of the rhodium salts, as in that of the iridium salts, the less soluble tri-strychnine salts are those of the *dextro*-rotary ions. In these cases also there is a strongly abnormal rotary dispersion; in the case of the iridium salt the Cotton effect was measured by Bruhat,[1] his results being in full agreement with those previously obtained with similar substances, and with the general behavior as described.

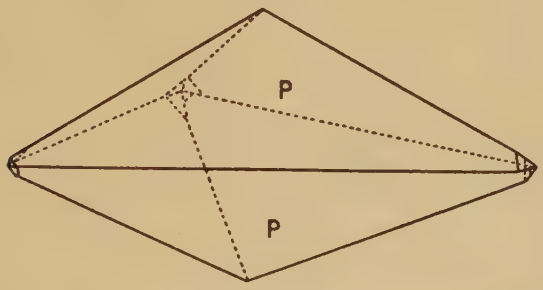


FIG. 35. Optically active Potassium trioxalato-iridiates.

The curves for the rotary dispersion are reproduced in Figure 36 and the corresponding data for the *dextro*-salts of rhodium and iridium are given in Table III.

According to Bruhat the specific rotation of the iridium salts is 0° at 4550 Å, and −100.1° at 4410 Å, −66.7° at 4390 Å, etc. The dispersion-curve thus takes on the form represented in Figure 36.

Longchambon[2] measured the rotary dispersion not only of the solution of *d*-potassium trioxalato-rhodiate, but also of the crystals themselves, which are transparent for wave-lengths between 4900 and 7700 Å, provided the plate is not over 0.16 mm. in thickness. While the dispersion-curve is shifted with respect to that of the solution, so

[1] G. Bruhat, *Bull. soc. chem.*, (4) 17, 223 (1915).
[2] L. Longchambon, *Compt. rend.*, 178, 1828 (1924); W. G. Burgers, Dissertation (Groningen, 1928).

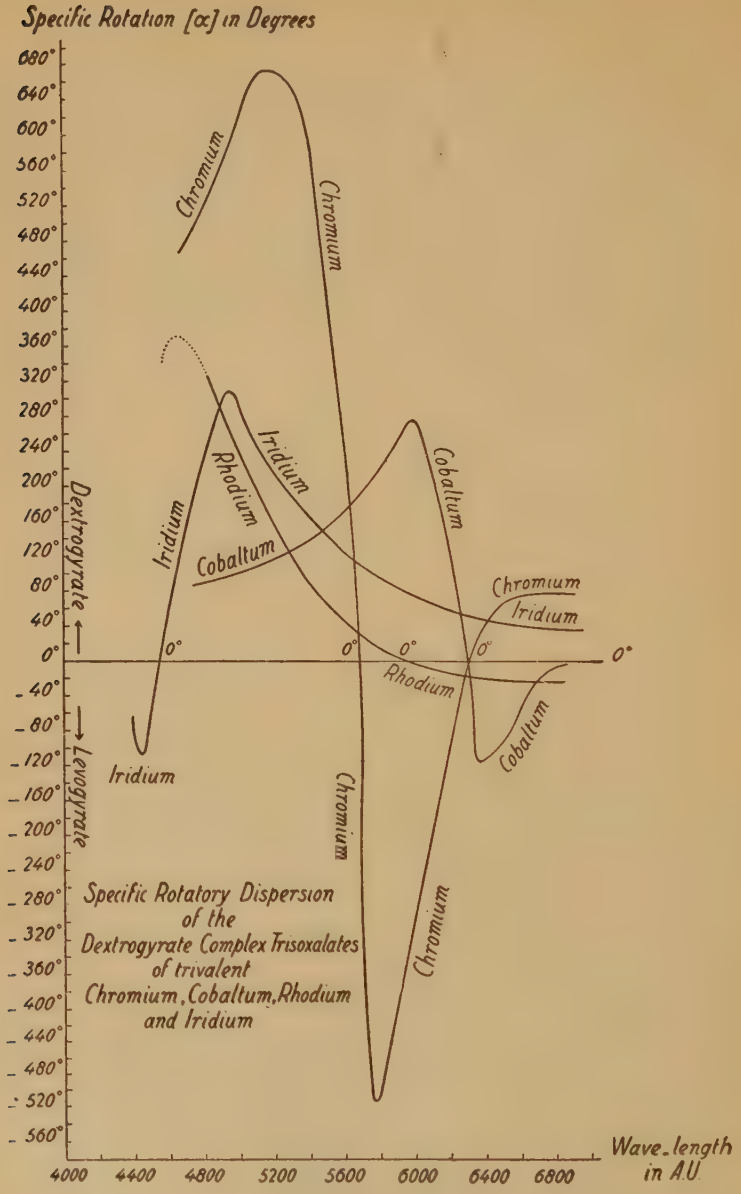

Specific Rotation [α] in Degrees
680°
640°
600°
560°
520°
480°
440°
400°
360°
320°
280°
240°
200°
160°
120°
80°
40°
0°
- 40°
- 80°
- 120°
- 160°
- 200°
- 240°
- 280°
- 320°
- 360°
- 400°
- 440°
- 480°
- 520°
- 560°
Dextrogyrate
Levogyrate
Chromium
Chromium
Iridium
Rhodium
Iridium
Cobaltum
Cobaltum
Chromium
Iridium
Rhodium
Cobaltum
Iridium
Chromium
Chromium
Specific Rotatory Dispersion of the Dextrogyrate Complex Trisoxalates of trivalent Chromium, Cobaltum, Rhodium and Iridium
4000
4400
4800
5200
5600
6000
6400
6800
Wave-length in A.U.

FIG. 36

TABLE III

Specific Rotations of Rhodium and Iridium Dextro-*Salts.*

Wave-length Å	Specific Rotation [α] *d*-Rh-Salt	*d*-Ir-Salt
4860	+ 344.3°	+ 270°
4950	+ 283.8	+ 308
5020	+ 245	+ 288
5100	+ 199.5	+ 251
5180	+ 166.7	+ 224
5260	+ 137.2	+ 200
5340	+ 110.6	+ 184
5420	+ 82.3	+ 161
5510	+ 65.0	+ 142
5605	+ 45.0	+ 122
5700	+ 29.2	+ 116
5800	+ 15.8	+ 86
5890	+ 6.0	+ 84
5900	+ 4.95	+ 81
5970	+ 0	+ 74
6030	− 4.38	+ 67
6140	− 11.1	+ 58
6260	− 16.5	+ 51
6380	− 20.3	+ 46
6520	− 22.8	+ 41
6660	− 24.3	+ 37
6800	− 25.2	+ 34
6945	− 26.6	+ 32.5

that it passes the zero axis at 5190 Å, he finds almost the same rotary dispersion as for the solution. For a plate 1 mm. in thickness he finds, for instance, the following values:

Å.U.:	4900	5000	5190	5200	5400	5600	5800
Rotation:	+51′	+28′	0′	−1′	−26′	−48′	−64′
Å.U.:	6000	6200	6400	6600	6800	7000	
Rotation:	−74′	−84′	−89′	−91′	−88′	−83′	

From these data he concludes that the molecules in the crystal are mutually parallel in orientation, the dispersion being due chiefly to their molecular anisotropism. Burgers,

TABLE IV

Observed rotations and ellipticities of a solution of the Potassium iridium salt (2 gm. of hydrated salt per 100 cu. cm.)

Wave-length Å	Rotation α (observed)	Ellipticity β
4390	− 8′	58′
4410	−12	—
4520	− 8	—
4530	− 2	60
4550	0	—
4600	+ 6	48
4650	—	42
4710	—	40
4760	23	—
4790	—	38
4800	26	—
4890	33	28
4910	35	—
4950	37	—
4960	—	23
4990	36	—
5020	—	19
5080	30	—
5120	29	14
5170	27	9.25
5230	25.6	6.4
5330	21.7	3.9
5490	—	2.7
5510	17.1	1.6
5530	—	1.45
5580	—	0.95
5740	12.1	—
5840	10.9	—
5850	—	0.30
5940	9.4	—
6060	7.95	—
6260	6.35	—
6460	—	0
6550	4.85	—
6940	—	0
6950	4.15	—

however, demonstrated by an X-ray analysis of their structure, that this conclusion is wrong, that the molecules are disposed helicoidally as in quartz, there being six molecules within an elementary cell. The rotary dispersion may be represented by a formula having three constants, one of them being negative; it is remarkably independent of the concentration of the solution, between 0.003 and 40 per cent.

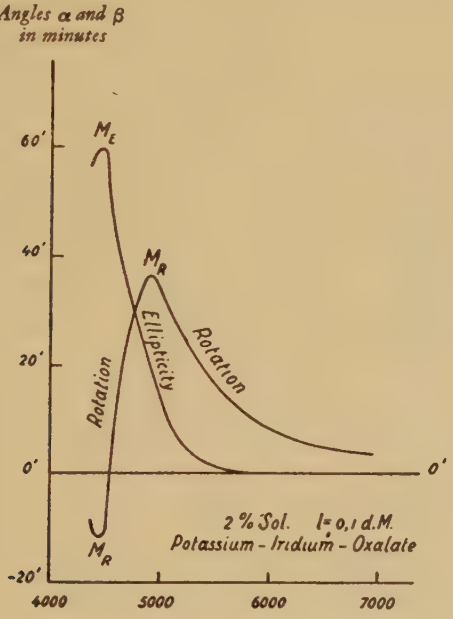


FIG. 37

Bruhat found the ellipticities given in Table IV for the potassium iridium salt in a solution containing two grams of the hydrated salt per 100 cu. cm. The results of the table are shown graphically in Fig. 37. They clearly demonstrate the divergent behaviors of the rotary dispersion and the ellipticity with respect to their zero and maximum values in the absorption band.

According to Délépine the iridium salt absorbs the whole violet and blue portions of the spectrum, and a part of the green.[1] The rhodium salt absorbs all the violet,

[1] M. Délépine, *loc. cit.*

blue and green, and a part of the orange. A one-per-cent solution absorbs all waves smaller than 5100 Å, so that there is undoubtedly a maximum and a zero value in this case also, accompanied by the Cotton effect, in that portion of the shorter wave-length region.

We have succeeded also in replacing the oxalic acid by malonic acid in the ions of the chromium and rhodium salts, and in splitting these potassium trimalanato-chromiates and rhodiates into their optically active

TABLE V

Approximate specific rotations for the Dipotassium hydrogen trimalonato-chromiate

Wave-length Å.	Observed specific rotation [α]
4860	+ 123.2°
5030	+ 156.5
5180	+ 177.1
5340	+ 153.8
5510	+ 74.3
5700	+ 23.6
6140	− 54.0
6380	− 23.6
6660	—

antipodes.[1] The reddish violet chromic salt is triclinic-pinacoidal, contains $3H_2O$, and therefore is not isomorphous with the corresponding ferric salt ($+4H_2O$). From the corresponding barium salt we obtain as the least soluble product a hydrogen distrychnine salt ($+2H_2O$) which is the salt of the *levo*-rotary trimalonato-chromiate ion. Here also the rapid racemization hinders the accurate measurement of the rotary dispersion. The approximate values given in Table V have been obtained for the dipotassium hydrogen trimalonato-chromiate. They are certainly too small, because the strychnine salt, which does not autoracemize so quickly, shows much higher values.

The zero value is reached at about 5750 Å, as in the case of the corresponding distrychnine hydrogen trimalonato-

[1] F. M. Jaeger, *Rec. trav. chim.*, 38, 294, 298, 300, 305, 309 (1919).

chromiate, whose rotations are about twice as great as those of the potassium salt, because it is more stable in solution. Here also the rotary dispersion is typically abnormal with a pronounced circular dichroïsm, exactly as in the case of the corresponding trioxalato-chromiate.

The racemic potassium trimalonato-rhodiate ($+3H_2O$) crystallizes in large orange colored well-developed crystals of monoclinic-prismatic symmetry (Figure 38).

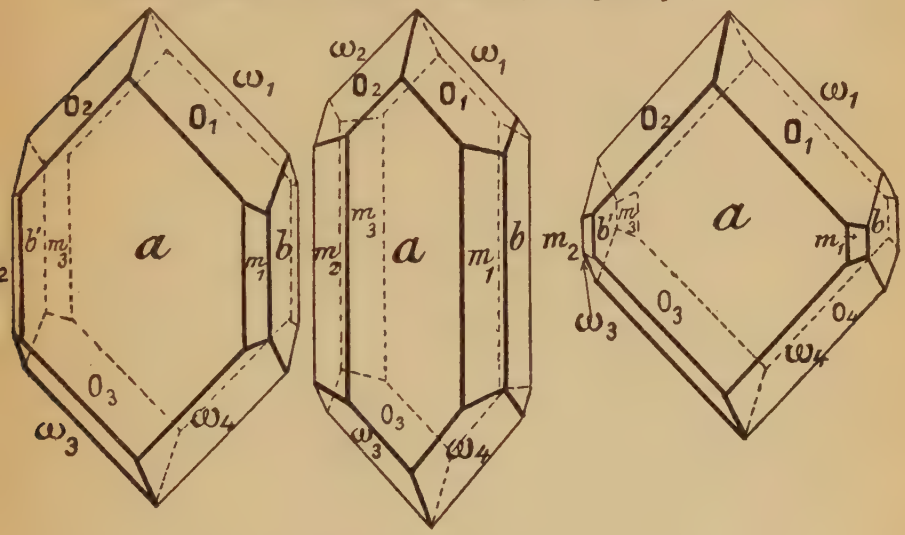


FIG. 38

Racemic Potassium trimalonato-rhodiate ($+3H_2O$)

The barium salt was treated with cinchonine sulphate; by fractional precipitation the least soluble orange-yellow cinchonine salt of the *levo*-rotary component is obtained first. It is remarkable that, notwithstanding the strong rotation of the ions, the cinchonine salts of both antipodes are *dextro*-rotary. The tricinchonine salt of the *dextro*-rotary ion contains $3H_2O$, that of the *levo*-rotary ion only $\frac{1}{2}H_2O$. If the cinchonine is removed from them as the iodide by means of potassium iodide, one obtains both antipodes in beautifully crystallized, but very soluble potassium salts. They both crystallize with $1\frac{1}{2}H_2O$ in the sphenoidal class of the monoclinic system (Fig. 39); their crystals are clearly

enantiomorphous, as required by Pasteur's law. The curve of the rotary dispersion is typically abnormal for wave-lengths shorter than 5800 Å, which is more remarkable since there is no absorption band observed in the vicinity of the wave-

TABLE VI

Rotations of Potassium trimalonato-rhodiate

Wave-length Å	Specific Rotations [α] of the *l*-Salt
4730	44°
4870	44
5020	44
5105	—
5180	46.2
5260	—
5340	46.9
5420	47.8
5515	47.8
5610	49.4
5700	50.5
5800	51.0
5910	48.9
6020	46.6
6140	46.3
6260	44.4
6380	44.0
6520	42.8
6660	43.9
6800	43.9

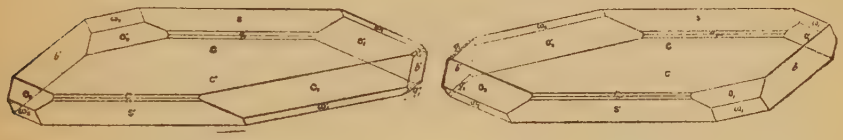
length where the rotation attains a maximum value. Table VI gives some of the rotations measured in this case.

We find almost an isochromatism in this special case (see Table VI).

This makes it seem somewhat problematical whether the existing theories on abnormal rotary dispersion in connection with the absorption phenomena, will be actually able to provide a rational explanation of this strange phenomenon, unless one here assumes that there are two

kinds of optically active ions in the solution.[1] It is evident, however, that these complex salts present a number of highly interesting physical phenomena and embrace a large number of additional problems, that still await final solution.

In conclusion we have an instance of a complex compound with a pentavalent central atom in the substance tripyrocatechyl-arsenic acid: $\{As^{V}(C_6H_4O_2)_3\}H + 5H_2O$,



Levo *Dextro*

FIG. 39. Potassium trimalonato-rhodiates $(+1\frac{1}{2}H_2O)$

and its splitting may here be noticed. This was accomplished with the aid of the cinchonine salts in a solution of 96-per-cent alcohol, the less soluble product being the *levo*-rotary acid. The *dextro*-rotary acid is best obtained by means of chinine ($C_{20}H_{24}O_2N_2$) or of cinchonidine ($C_{19}H_{22}O_1N_2$). For sodium light the specific rotation $[\alpha]$ of the ion is about 446°, that of the potassium salt $(+1H_2O)$ is about 460°. Undoubtedly the analogously-built derivatives of titanium, silicon, zirconium, with salicylic acid and with pyrocatechol, prepared by Rosenheim and Sorge, will also be resolved into their optically-active components if favorable conditions are realized.

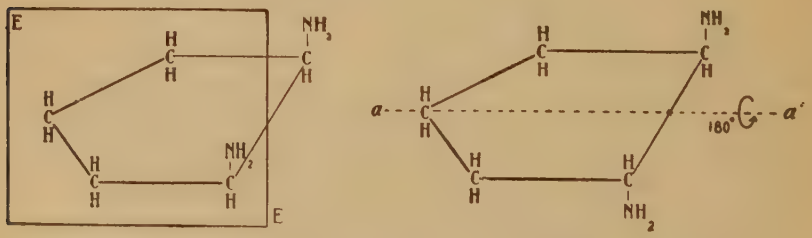
[1] P. Drude, *Lehrbuch der Optik*, p. 382 (1900).

CHAPTER IX

Introduction of Antipodal Components

We now pass to a consideration of the phenomena that present themselves when we introduce components, that may occur in optical antipodes, into salts of the tri-diammino or tri-biacido types. The study of these cases has revealed a number of highly interesting facts both optical and chemical. The phenomena considered may be illustrated by an investigation, recently published by us, into the complex salts of cobalt and rhodium of the triethylene-diamino type, in which one, two or three molecules of the base are successively replaced by a corresponding number of molecules of *trans*-1,2-cyclopentylene-1,2-diamine, a hitherto unknown base now available which, in this one of its two possible isomers, can be readily split into its potical antipodes. As may be anticipated, circumstances will be much more complicated in cases of this kind because the influence of the substituted optically-active molecules or radicals is now superimposed upon that of the enantiomorphous configurations of the complex ions.

The new base itself, which was used in these experiments, evidently may occur in two isomeric forms, namely, a *cis*- and a *trans*-configuration:



cis *trans*

Fig. 40

Of these forms only the *trans*-base has been obtainable hitherto, although many attempts were made to prepare

the *cis*-base and to derive it by transformation from the *trans*-base. On the other hand, only the *trans*-base can be split into optically active antipodes, because its sole symmetry element is a single binary axis of rotation lying in the plane of the ring; while the *cis*-form has a plane of symmetry perpendicular to the plane of the ring and hence must be identical with its mirror image.

It was possible to split *trans*-1,2-cyclopentylenediamine by the aid of *d*- and *l*-tartaric acid; the bitartrates were prepared and separated by fractional crystallization. If *d*-tartaric acid is used, the *d*-tartrate of the *levo*-gyrate base appears to be the least soluble salt. In this way the pure *d* and *l* bases were obtained, their specific rotation $[\alpha]$ being about $\pm 37.7°$, for $\lambda = 7000$ Å, and increasing steadily to about $\pm 114°$, for $\lambda = 4200$ Å. All the salts were prepared by means of the racemic base (*r*) and its antipodes *d* and *l*.

Besides obtaining an answer to the question as to what changes are caused in the rotary dispersion of the optically active complex ions of this type by the gradual replacing of one, two or three molecules of ethylenediamine with the *d*- and *l*-cyclopentylenediamine molecules, it also appeared to be of great interest to determine the number of possible isomerides and their spatial arrangements. The substituted molecules possess a binary symmetry axis, as do the ethylenediamine molecules; but in distinction from ethylenediamine, they are dissymmetrical and optically active and it might be possible, therefore, that their admission to the dissymmetrical configuration of the ion would be impeded to a certain degree by sterical hindrances.

Even in the simplest cases—where all three ethylenediamine molecules of the complex cobalt or rhodium cations are replaced by three molecules of the optically active base—the reaction may lead to a considerable number of isomers if one uses the racemic base which, in solution, acts as a $(d + l)$-base. If we indicate the *dextro*- and *levo*-rotary components by *d* and *l*, respectively, the racemic base by *r* and the *dextro*- and *levo*-rotary configurations of the ions themselves by D and L—then the

action of three molecules of the racemic base, being such that only an odd number of *d* and *l* molecules can enter the complex ions, may lead theoretically to the following eight combinations:

$\{ddd\}_D$; $\{lll\}_L$; $\{ddd\}_L$; $\{lll\}_D$; $\{ddl\}_D$; $\{ddl\}_L$; $\{dll\}_D$; $\{dll\}_L$;

provided there are no special reasons *a priori* why one of these combinations should be impossible. Moreover, since these eight cases, when taken in pairs, represent each other's mirror images, for example, $\{ddd\}_D$ and $\{lll\}_L$, $\{ddl\}_D$ and $\{dll\}_L$, etc.,—the said derivatives may be combined pair-wise in equimolecular quantities, thus yielding four racemoids and twenty-four partial racemoids.

It is worth noting here that all such cations having three identical molecules present—also the case in the triethylenediamino complexes mentioned—will possess the rather high degree of symmetry D_3 (the symmetry of *d*- and *l*-quartz), provided the substituents themselves have a single binary symmetry axis. In other cases, such as $\{ddl\}$, this degree of symmetry of the cation must be much less even if the condition just mentioned be fulfilled. In this case the complex ions will have but a single polar binary axis A_2. In both cases, however, these complex ions may be separated into different mirror images, because their symmetry is always purely axial.

When we turn to consider the complex rhodium salt obtained in the reaction between racemic *trans*-1,2-cyclopentylenediamine and crystalline sodium hexachlororhodiate (hydrated and powdered), we seem to have the simplest conditions. The same reaction can be carried out subsequently with each of the two antipodes of the base; the products thus obtained permitting direct comparison with the previous ones.

On treating the solid $Na_3\{RhCl_6\} + 9H_2O$ with the racemic base there was obtained, in addition to a small quantity of an alcohol-soluble orange-colored by-product,[1]

[1] On treating the orange-colored by-product with NaI there resulted an intensely orange-colored iodide. When an alcoholic solution of this iodide was heated, it gradually decomposed with the precipitation of the ordinary white iodide mentioned above. Analysis showed that there is here present a double compound consisting of two molecules of the white iodide and one molecule of a non-ionogenic complex containing Rh, Cl, alcohol, and cyclopentylenediamine.

only a single white crystalline product readily precipitated as a colorless iodide by means of NaI, and from which a whole series of other salts could be prepared by means of different silver salts. The iodide obtained had the composition[1] $\{Rh(Cptdin)_3\}I_3 + H_2O$.

By converting the corresponding chloride (which crystallizes with $2H_2O$) by means of Ag-*d*-tartrate or Ag-*l*-tartrate, into the corresponding chlorotartrates, it was possible to prove that the original salt is a true racemic compound from which two optically-active antipodes could be separated. If Ag-*d*-tartrate was used, the less soluble fraction of the chloro-*d*-tartrates thus obtained gave a chloride whose solution appeared to be strongly *levo*-rotary. Careful fractional crystallization and the determination of the complete curves of the rotary dispersions of these fractions enabled us to prove, with certainty, that no other components than the *dextro*-rotary and *levo*-rotary salts mentioned were present in the original reaction product.

In the same reaction, if only the *d*- or the *l*-base were used then in each case only a single optically-active product appeared to result. The accurate measurement of the rotary dispersions of the two salts, and their comparison with the products of the splitting of the racemic compound mentioned, made it perfectly certain that the *levo*-rotary complex cation had only three molecules of the *d*-base, and that the *dextro*-rotary complex cation had only three molecules of the *l*-base. The reaction between the racemic cyclopentylenediamine and $Na_3\{RhCl_6\} + 9H_2O$ generated no other salts than those of the ions $\{Rh^{III}(lll)\}_D^{\cdots}$ and $\{Rh^{III}(ddd)\}_L^{\cdots}$. The observed rotations are collected in Table VII.

The complete curve of the rotary dispersion of these salts is represented in Figure 41.

From the foregoing it must be concluded: that the *levo*-rotary configuration of the complex ion is incompatible with the presence of three *levo*-molecules of the base; and similarly, that the presence of three *dextro*-rotary mole-

[1] (Cptdin) is here used as a convenient abbreviation for cyclopentylenediamine.

TABLE VII

Rotary Dispersion of d-$\{Rh^{III}(l\text{-Cptdin})_3\}Cl_3 + 4H_2O$

Wave length Å	Rotation Observed α	Specific Rotation $[\alpha]$	Molecular Rotation $[M].10^{-2}$
7002	+ 1.06	+ 265°	+ 1541°
6737	+ 1.12	+ 280	+ 1628
6494	+ 1.21	+ 302	+ 1756
6273	+ 1.32	+ 330	+ 1919
6073	+ 1.40	+ 350	+ 2035
5893	+ 1.52	+ 380	+ 2210
5732	+ 1.61	+ 402	+ 2338
5590	+ 1.71	+ 428	+ 2489
5463	+ 1.81	+ 452	+ 2628
5346	+ 1.91	+ 480	+ 2791
5237	+ 2.02	+ 505	+ 2937
5135	+ 2.13	+ 532	+ 3093
5040	+ 2.25	+ 562	+ 3268
4952	+ 2.35	+ 588	+ 3419
4870	+ 2.45	+ 612	+ 3559
4794	+ 2.56	+ 640	+ 3722
4723	+ 2.65	+ 662	+ 3849
4657	+ 2.75	+ 687	+ 3995
4595	+ 2.84	+ 710	+ 4129
4537	+ 2.96	+ 740	+ 4303
4482	+ 3.04	+ 760	+ 4419
4430	+ 3.13	+ 782	+ 4547
4381	+ 3.24	+ 810	+ 4710
4335	+ 3.30	+ 825	+ 4797
4291	+ 3.37	+ 842	+ 4896
4249	+ 3.41	+ 852	+ 4954

cules of the base is incompatible with the *dextro*-rotary configuration of the complex rhodium ion.

The racemic perchlorate, which forms anhydrous crystals, was observed to split into its antipodes by spontaneous crystallization of the solutions at room temperature. The crystals deposited (+ $12H_2O$) were octahedral and when selectively sorted and individually dissolved, their solutions were respectively *dextro*- and *levo*-rotary. The determinations of the solubilities of the racemic compound

and its antipodes show that we here had spontaneous crystallization of the racemoid at a minimum transformation temperature of 48°, this form becoming the more stable

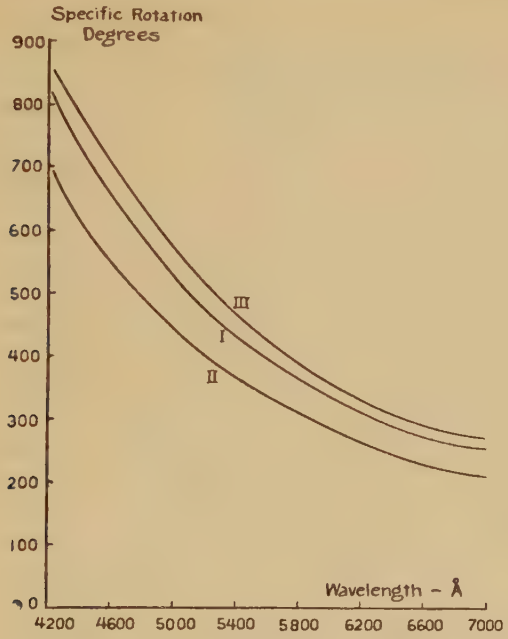


FIG. 41

phase with respect to the antipodes above this temperature. The transformation may be represented by

$$d\text{-}[\{Rh^{III}(Cptdin)_3\}(ClO_4)_3 + 12H_2O] +$$

$$l\text{-}[\{Rh^{III}(Cptdin)_3\}(ClO_4)_3 + 12H_2O] \overset{48^\circ}{\rightleftarrows}$$

$$\text{racem.}[\{Rh^{III}(Cptdin)_3\}(ClO_4)_3] + 24H_2O.$$

Therefore the splitting of the anhydrous racemoid in solution, into the highly hydrated antipodes evidently is accompanied by an evolution of heat, in harmony with the theorem of mobile equilibrium. The graphs of Figure 42 represent the solubility relations that exist in this reaction.

The phenomena observed in the case of the corresponding cobalt salts are quite analogous to those of the rhodium

salts. Here also three molecules of the *d*-base are able to enter only the *levo*-rotary configuration of the complex ion, and three molecules of the *l*-base can enter only the *dextro*-rotary ion. In both cases there is the question of a "partially asymmetrical" synthesis: the dissymmetrical arrangement in the complex ion has a strongly selective directing influence upon the substitutes, so that only a special con-

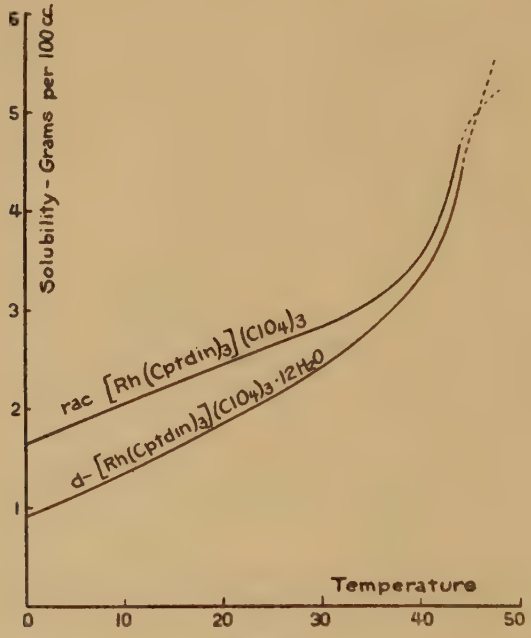


FIG. 42

figuration of these is permissible and the other one is excluded. This same fact has been observed in other cases. Smirnoff[1] found this phenomenon when he introduced optically active 1,2-propanediamine into the complex ions of this type having cobalt and platinum as central atoms. In this case as well as in the analogous ones studied by Tschugaeff and Sokoloff,[2] the complex salts obtained always had rotations opposite in sign to those of the optically-active substitutes introduced into the complex ion.

[1] A. P. Smirnoff, *Helv. Chim. Acta*, 3, 177 (1920).
[2] L. Tschugaeff and W. Sokoloff, *Ber.*, 40, 177 (1907); 42, 56 (1909).

We shall soon see, however, that this partially asymmetrical synthesis is by no means a common phenomenon; there may be circumstances under which the optically-active substitute can enter the one as well as the enantiomorphous configuration of the complex ion.

In the case of the rhodium salt as well as in that of the cobalt salt, it was observed that the less soluble combinations were the chloro-*d*-tartrates of the *levo*-rotary complex ions and the chloro-*l*-tartrates of the *dextro*-rotary ones, so that these are the first ones deposited in fractional crystallization. It is thus directly proved that the rhodium and cobalt salts having the same configuration show rotations of the same sign. Werner's conclusion that the substitution of rhodium for cobalt in complex ions of analogous constitution would invert the sign of rotation,[1] is wrong, as has already been pointed out. His arguments based upon the relative solubilities of compounds derived from the same optically-active base or acid used in splitting the racemoid, have been proved invalid by the experience of later years, as has been emphasized by Meisenheimer.[2] The phenomena we have observed can but reinforce our arguments against Werner's views.[3] No doubt can remain today that cobalt and rhodium salts of analogous configuration and constitution deflect the plane of polarization of incident light in the same direction.

The perchlorate of the cobaltic ion agrees with that of the corresponding rhodium ion in showing a spontaneous splitting into its antipodes when crystallizing at room temperature. Here also the transition temperature—if it really exists—must be a minimum temperature for the racemoid and occur in the vicinity of $-1.5°$. This is clearly demonstrated by the results of the solubility determinations shown in Figure 46.

It is impossible to measure directly this transition temperature, because at such low temperatures the solubilities are so very slight that the actual depression of the freezing point is too small to permit the simultaneous

[1] A. Werner, *Ber.*, 45, 1229 (1912).
[2] J. Meisenheimer and collab., *Ann.*, 449, 190 (1926).
[3] F. M. Jaeger, *Rec. trav. chim.*, 38, 170 (1919); *Chem. Weekblad*, 14, 728 (1917); *Proc. Acad. Sci. Amsterdam*, 20, 264 (1917); *Principle of Symmetry*, p. 251ff (1920).

appearance of a liquid and a solid phase; the whole mass is converted into a solid mixture of ice and salt.

We must conclude that at all temperatures above 0° the optically-active octahedral crystals must be metastable

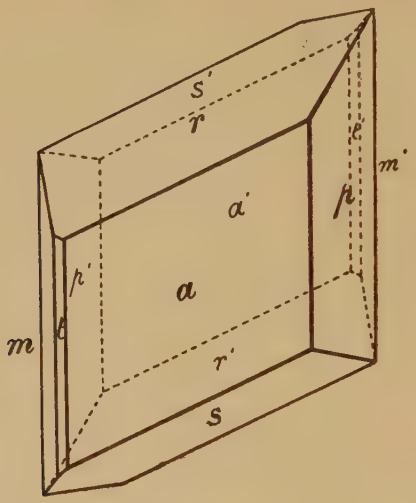


FIG. 43. $\{Co(Cptdin)_3\}Cl_3 + 3H_2O$

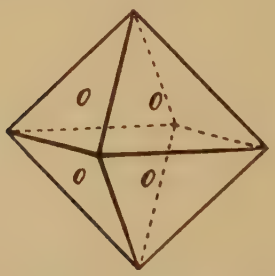


FIG. 44. *d*-$\{Co(l\text{-}Cptdin)_3\}Cl_3 + 4H_2O$

with respect to the racemic compound. It is very remarkable, therefore, that these octahedral crystals are nevertheless deposited in the inactive solution at room temperature. Ostwald remarked a long time ago that within a field of stability of some phase, the primary deposit often is not the stable phase but a metastable form, and this phenomenon has been observed in several cases. If the saturated

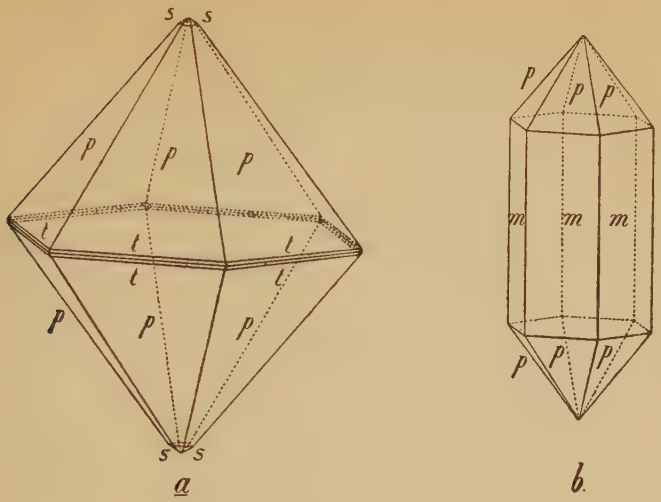


FIG. 45. Hexagonal form of
$\{Co(l\text{-Cptdin})_3\}Cl_3 + 3H_2O$

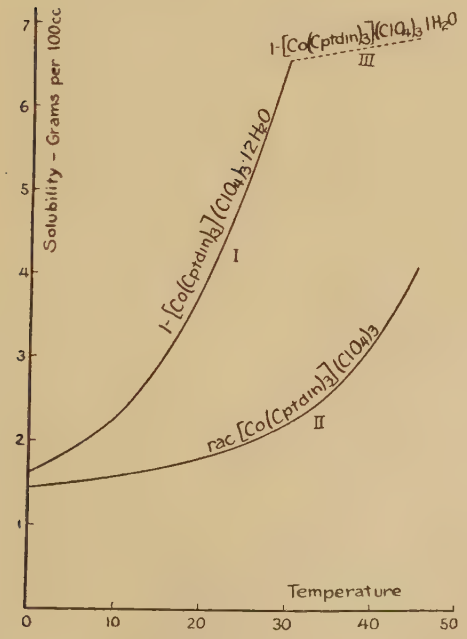


FIG. 46

TABLE VIII

Rotary dispersion of $Co^{III}(l\text{-Cptdin})_3Cl_3+4H_2O$.

(The red-orange solution contained 0.4 gm per 100 cu. cm; tube length = 10 cm; mol. wt. = 520)

Wave-length Å	Rotation Observed α	Specific Rotation $[\alpha]$	Molecular Rotation $[M].10^{-2}$
7002	+ 1.38	+ 345	+ 1794
6737	+ 1.52	+ 380	+ 1976
6494	+ 1.70	+ 425	+ 2210
6273	+ 1.86	+ 465	+ 2418
6073	+ 1.96	+ 490	+ 2548
5893	+ 2.06	+ 515	+ 2678
5732	+ 2.19	+ 547.5	+ 2847
5590	+ 2.38	+ 595	+ 3094
5463	+ 2.96	+ 740	+ 3848
5346	+ 3.76	+ 940	+ 4888
5237	+ 4.66	+ 1165	+ 6058
5135	+ 5.34	+ 1335	+ 6942
5042	+ 5.64	+ 1410	+ 7332
5000	—	+ 1420 M_1	+ 7384
4950	+ 5.62	+ 1405	+ 7306
4870	+ 5.16	+ 1290	+ 6708
4794	+ 4.70	+ 1175	+ 6110
4723	+ 3.76	+ 940	+ 4888
4657	+ 3.28	+ 820	+ 4264
4595	+ 3.02	+ 755	+ 3926
4537	+ 2.82	+ 705	+ 3666
4482	+ 2.62	+ 655	+ 3406
4430	+ 2.70	+ 675 M_2	+ 3510
4381	+ 2.62	+ 655	+ 3406
4335	+ 3.02	+ 755	+ 3926
4291	+ 3.40	+ 850	+ 4420
4249	+ 3.66	+ 915	+ 4758
4209	+ 3.96	+ 990	+ 5148

solutions be inoculated with a nucleus of the crystallized racemic salt the octahedral crystals gradually disappear, giving place to those of the racemic compound, thus proving that the components are really metastable with respect to the racemic compound under these conditions.

The color of these cobalto salts is highly remarkable: being pink—as true cobalt salts in solution—instead of having the deep orange or blood red color of the tri-[ethylenediammino]-cobaltic salts. The iodide, however, forms an exception to this rule and shows the true color of the luteo series.

The specific and molecular rotations of these cobalt and rhodium salts are many times greater, for the same wave length, than are those of the corresponding tri[ethylenediammino] salts. The absolute values of these specific rotations in the case of the cobaltic salts are three to ten times greater, and in the case of the rhodium salts seven to eight times greater, than for the corresponding salts of the tri-[ethylenediammino] series. On the other hand, the rotary dispersion of the rhodium salts in either case does not differ to the same degree as the rotations themselves. The rotary dispersion of the cobalt salts of this type is highly abnormal, because of the strong absorption in the visible portion of the spectrum (Table VIII). Circular dichroïsm (Cotton effect) is present also. Figure 47 gives the dispersion curve of the *dextro*-rotary chloride and the corresponding curve for d-$\{Co^{III}(d\text{-Propin})_3\}Br_3 + 2H_2O$.

The crystal forms of the analogous cobalt and rhodium salts appear to be quite analogous; they are even completely isomorphous if their water content is the same. The optically-active chlorides ($+4H_2O$), nitrates ($+4H_2O$), chlorates ($+12H_2O$), and perchlorates ($+12H_2O$), all crystallize in beautiful octahedral crystals of pentagonal-icositetrahedral symmetry (Figure 48). In the case of the chlorides and nitrates we also met with hydrates having $3H_2O$, which are formed in the solution at somewhat higher temperatures and have a hexagonal-bipyramidal symmetry (Figure 49). The particular symmetry of these crystals has been confirmed in each case by Röntgen-spectroscopic investigations of their structures.

The phenomena are much more complicated if in addition to cyclopentylenediamine one tries to obtain complex salts of cobalt whose cations also contain one or two molecules of ethylenediamine.

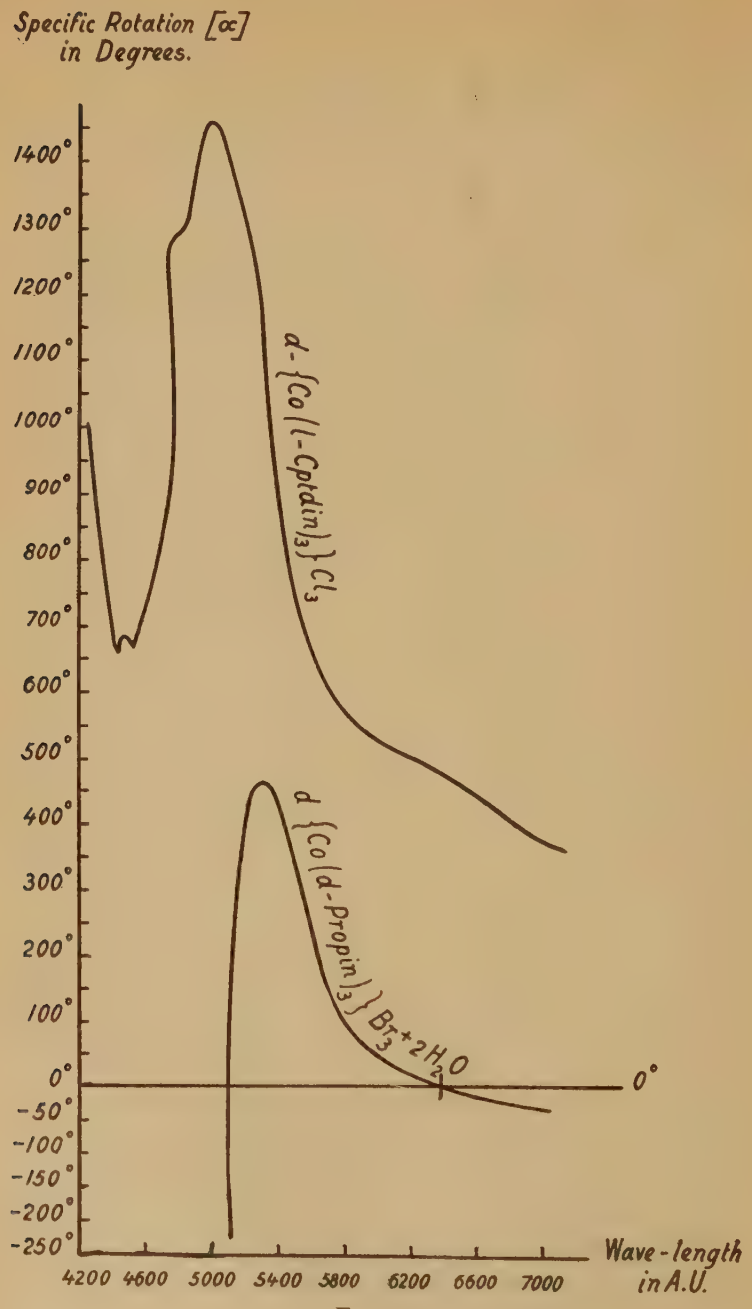

Specific Rotation [α]
in Degrees.
1400°
1300°
1200°
1100°
1000°
900°
800°
700°
600°
500°
400°
300°
200°
100°
0°
-50°
-100°
-150°
-200°
-250°
d-{Co(l-Cptdin)3}Cl3
d{Co(d-Propin)3}Br3+2H2O
0°
4200 4600 5000 5400 5800 6200 6600 7000
Wave-length
in A.U.

FIG. 47

The preparation of salts of the type $\left\{\begin{matrix}Co^{III}(Ene)_2\\(Cptdin)\end{matrix}\right\}X_3$ may start with the green praseo-, or the pink chloro-aquo-

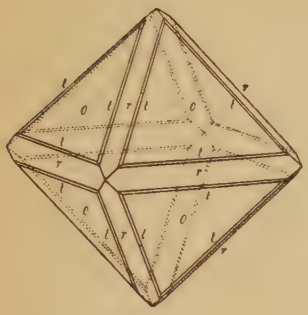


FIG. 48

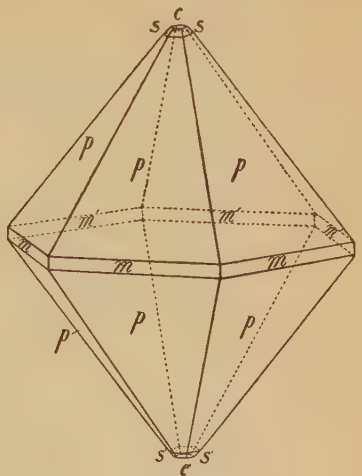
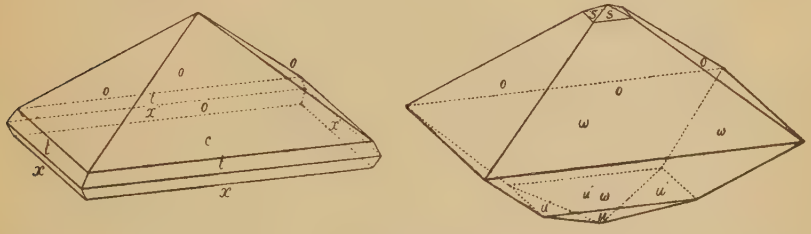


FIG. 49

cobaltic salts containing two molecules of ethylenediamine in their complex ions. If salts like $\left\{\begin{matrix}Co^{III}(Ene)_2\\Cl_2\end{matrix}\right\}Br$ or $\left\{\begin{matrix}Co^{III}(Ene)_2\\Cl\\H_2O\end{matrix}\right\}Br_2$ are treated with racemic or with *d*-



a *b*

FIG. 50

Racemic $\left\{\begin{matrix}Co^{III}(Ene)_2\\(Cptdin)\end{matrix}\right\}I_3$

and *l*-cyclopentylenediamine, salts of the type desired are actually formed. In the simplest case one molecule of the

racemic base is used; an optically inactive salt having the color of the ordinary tri[ethylenediammino]-cobaltic salts, is then produced; and it appears to be a true racemic com-

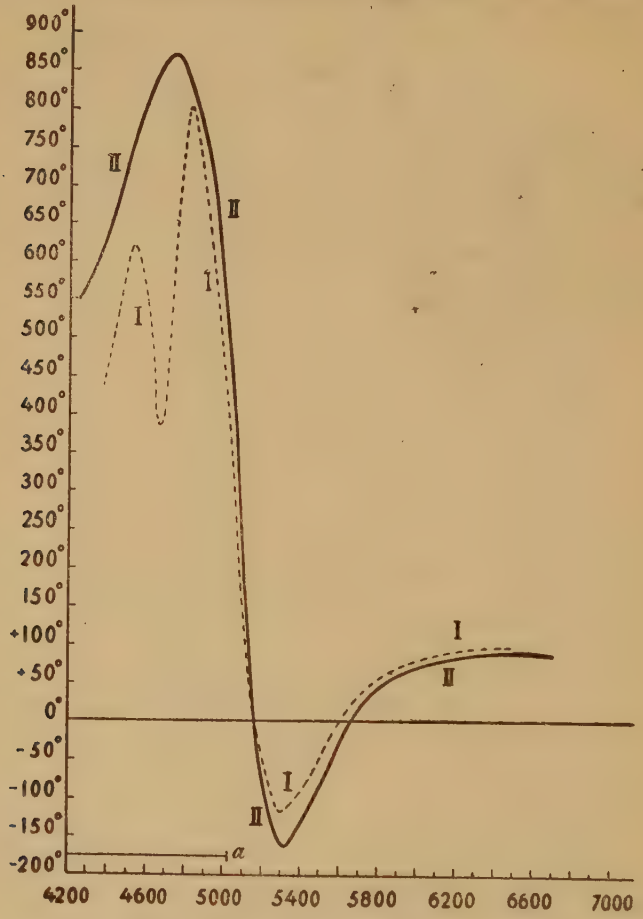


FIG. 51

pound since it may be split into two optically active antipodes by means of the bromo-*d*-, and the bromo-*l*-tartrates, respectively. Its crystal form seems to be shown by Figure 50.

The dispersion curve (II) of the bromide prepared from the less soluble bromo-*d*-tartrate, is shown graphically in Figure 51 and in detail in Table IX.

TABLE IX

Rotary dispersion of d-$\left\{\begin{matrix}Co^{III}\,(Ene)_2\\(Cptdin)\end{matrix}\right\}Br_3 + 2\,H_2O$.

(Solution = 0.4 gm. salt in 100 cu. cm.; tube length = 10 cm.; mol. wt. = 555)

Wave-length Å	Rotation observed, α	Specific Rotation, $[\alpha]$	Molecular Rotation [M]
6737	+ 0.35	+ 87.5°	+ 486°
6464	+ 0.35	+ 87.5	+ 486
6273	+ 0.34	+ 85	+ 470
6073	+ 0.28	+ 75	+ 414
5893	+ 0.22	+ 55.5	+ 307
5732	+ 0.08	+ 20	+ 110
5675	0	0	0
5590	− 0.17	− 42.5	− 235
5463	− 0.45	− 112.5	− 626
5346	− 0.64	− 160	− 885
5324	—	− 162	− 895
5237	− 0.36	− 90	− 497
5185	0	0	0
5135	+ 0.295	+ 74	+ 408
5040	+ 2.02	+ 505	+ 2791
4952	+ 2.80	+ 700	+ 3870
4870	+ 3.16	+ 790	+ 4367
4794	—	+(860)?	—
4723	—	+(874)?M	+(4831?)
4657	+ 3.34	+ 835	+ 4616
4595	+ 3.18	+ 795	+ 4395
4537	+ 3.02	+ 755	+ 4172
4482	+ 2.78	+ 695	+ 3842
4381	+ 2.48	+ 620	+ 3427
4335	+ 2.34	+ 585	+ 3234
4291	+ 2.26	+ 565	+ 3112

This bromide was shown to have the constitution of $\left\{\begin{matrix}Co^{III}(Ene)_2\\(l\text{-Cptdin})\end{matrix}\right\}Br_3 + 2H_2O$. The other component gave the same rotations, but with opposite signs. The difference between the dispersion-curve for this salt (Table IX) and that of the salt of the ion $\{Co^{III}(l\text{-Cptdin})_3\}_D$ is very clear,

as is shown by a comparison of Figures 47 and 51. The only feature common to the two curves is the high peak near their absorption band, which in the case of the latter salt is at about 4950 Å and for the newly prepared salt, $\left\{\begin{matrix}\{Co^{III}(Ene)_2 \\ (l\text{-Cptdin})\}_D\end{matrix}\right\}Br_3$ is at about 4800 Å. The most typical difference between the two curves occurs at the second crossing of the axis of zero rotation; this takes place at about 5200 Å for the latter case and at 5700 Å in the former case.

If in the reaction indicated above the *levo*-rotary component is used in place of the racemic base, there results an optically-active product showing a rotary dis-

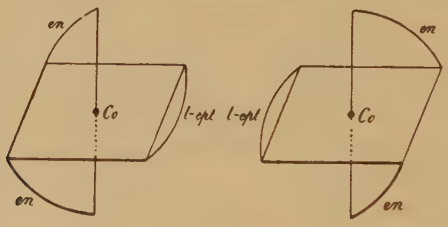


FIG. 52

persion quite different from that reproduced in Figure 51. In the first place its specific rotation is much less: curve I in Figure 53 gives the observed values. On closer examination it was found that there is here formed a kind of optically-active, partially racemic compound consisting of two optically-active components that are no longer each other's mirror images. With the aid of *d*-tartaric acid we succeeded in separating from this product a bromo-*d*-tartrate, whose rotary dispersion appeared to be the same as that of the bromo-*d*-tartrate prepared from the bromide (see Figure 51). Thus it seems to be certain that one of the components of the partially racemic compound is a salt derived from the ion: $\left\{\begin{matrix}\{Co^{III}(Ene)_2 \\ (l\text{-Cptdin})\}_D\end{matrix}\right\}^{\cdots}$

The very unfavorable solubility relations of the two components—even when other substances such as mandelic acid, malic acid, bromocamphorsulphonic acid, were used—made it seem impossible to obtain the second com-

ponent in a perfectly pure state, but there can be no doubt of the fact that this component is a derivative of the ion $\left\{\begin{matrix}Co^{III}(Ene)_2 \\ (l\text{-Cptdin})\end{matrix}\right\}_L^{\cdots}$, which indeed is not the mirror image of the first (Fig. 52).

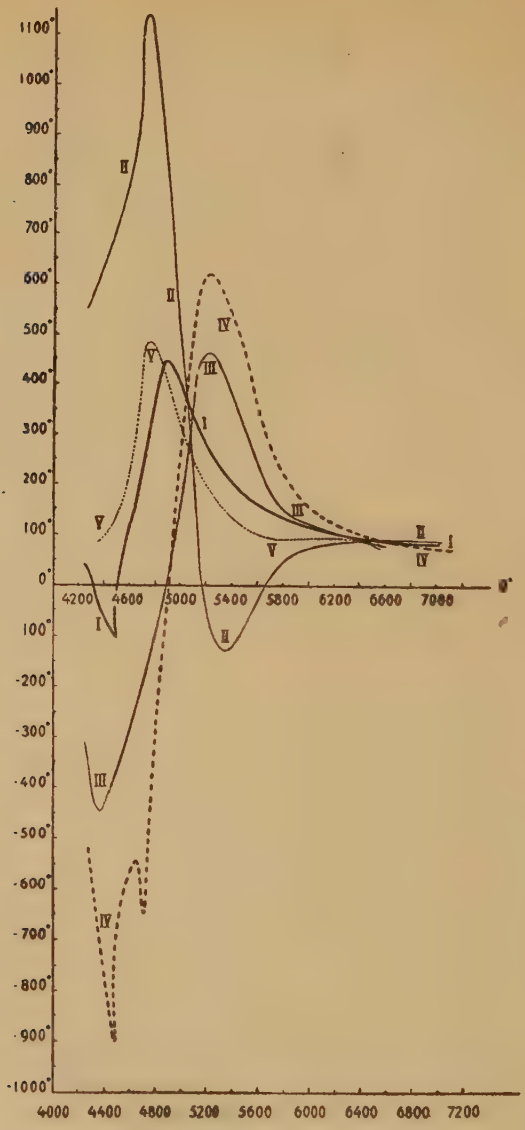
We have reproduced in Figure 53, Curve III, the plotted observed rotary dispersions of this impure second component; while Curve IV indicates the theoretical calculated dispersion-curve of the same component in the pure state. Curve IV was obtained by combining Curves I and II, the latter being the true dispersion-curve of the pure first component. Finally Curve V of this figure represents the rotary dispersions of the partially racemic compounds, as derived from the combination of Curves II and III; the analogy with Curve I is evident, although the inaccuracies in Curve III undoubtedly cause deviations from the true form of Curve I.

In the same way the reaction between *d*-cyclopentylenediamine and the original praseo-(violeo-)salt gives a partially racemic compound consisting of salts derived from the cations:

$$\left\{\begin{matrix}Co^{III}(Ene)_2 \\ (d\text{-Cptdin})\end{matrix}\right\}_L^{\cdots} \text{ and } \left\{\begin{matrix}Co^{III}(Ene)_2 \\ (d\text{-Cptdin})\end{matrix}\right\}_D^{\cdots}$$

Had it been possible for us to secure each of these four components in a perfectly pure condition, we would have been able to obtain in addition to four partially racemic compounds, also the two optically inactive true racemic compounds by combining the antipodes pairwise in equimolecular quantity, and also a racemoid containing all four components.

In the preparation of salts of the type $\left\{\begin{matrix}Co^{III}(Ene) \\ (Cptdin)_2\end{matrix}\right\}X_3$, we start with the praseo-(violeo-)salts of the formula $\left\{\begin{matrix}Co^{III}(Cptdin)_2 \\ Cl_2\end{matrix}\right\}Cl$. The cobaltic salts are obtained by oxidizing with hydrogen peroxide. A solution of 7.5 gm. of $CoCl_2$ in 25 cu. cm. of water is mixed in a wide flask, with 5 gm. cyclopentylenediamine, to which we slowly add


1100°
1000°
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4200
4600
5000
5400
5800
6200
6600
7000
4000
4400
4800
5200
5600
6000
6400
6800
7200
I
II
III
IV
V

FIG. 53

60 cu. cm. of a 10-per-cent solution of H_2O_2. It was found that oxidation with an air current does not give good results. When the reaction is finished we add 100 cu. cm. of strong HCl to the solution and the liquid is then heated on a water-bath. The praseo-salt soon begins to precipitate. The latter is filtered off from the mother liquor and washed with alcohol and ether until a completely neutral reaction is obtained. The yield of praseo-salt is about 6.2 gm. The mother liquor still contains some salt of the composition $\{Co^{III}(Cptdin)_3\}Cl_3$, which may be precipitated as the iodide. In subsequent experiments we used the racemic

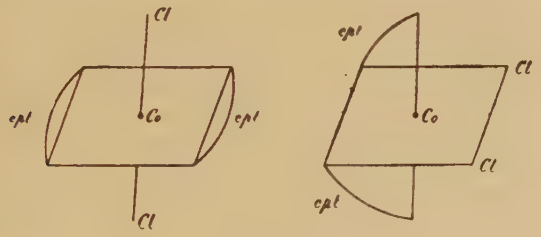


FIG. 54

base, or one of its optically active antipodes, for this reaction and it seems to be possible to obtain the following salts:

$$\left\{\begin{matrix} Co^{III}(d\text{-Cptdin}) \\ (l\text{-Cptdin}) \\ Cl_2 \end{matrix}\right\} Cl + 2H_2O; \left\{\begin{matrix} Co^{III}(d\text{-Cptdin})_2 \\ Cl_2 \end{matrix}\right\} Cl + 2H_2O;$$

and $\left\{\begin{matrix} Co^{III}(l\text{-Cptdin})_2 \\ Cl_2 \end{matrix}\right\} Cl + 2H_2O$. The two last-mentioned, bluish-green praseo-salts are optically active; their molecules differ from their own mirror images, but of course they can not be individually separated. The curve of rotary dispersion of this praseo-salt is reproduced in Figure 55 together with that of the corresponding violeo-salt which is obtained by gently heating the solutions of the praseo-salts. (See also Tables X and XI). The praseo-salt (I) (Figure 53) first mentioned cannot be split into its antipodes, because its cation has a plane of symmetry perpendicular to the plane containing the two molecules of

the base (Figure 56). This optically inactive salt must differ, therefore, from the true racemic compound II obtained by mixing an equimolecular quantity of the second

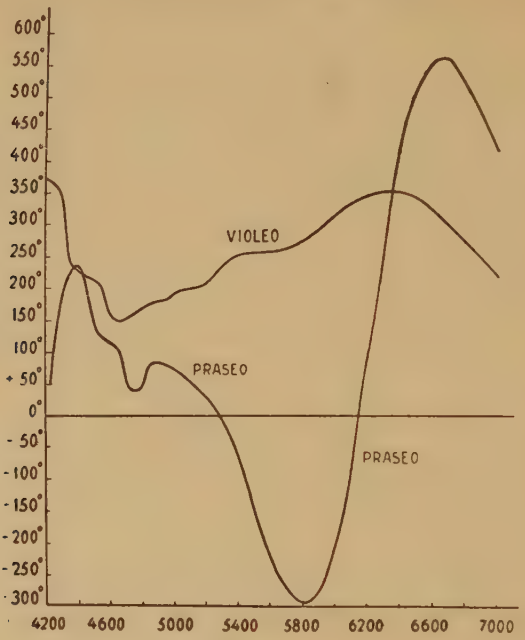


FIG. 55

and third, and letting them crystallize out from the mixed solutions. Experience, however, taught us that this racemic compound is not in any way distinguishable from

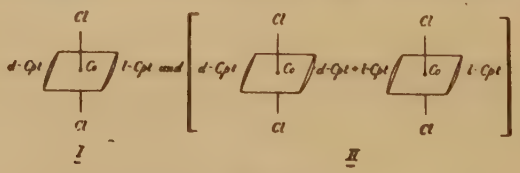


FIG. 56

the salt prepared from the racemic base. Evidently the true racemic salt also is generated in this last reaction, so that the first of the three formulas in Figure 56 may be excluded in advance.

TABLE X

Rotary Dispersion of Praseo-$\left\{\begin{matrix}Co^{III}(l\text{-Cptdin})_2\\Cl_2\end{matrix}\right\}Cl$.

(Solution of 0.4 gm. salt in 100 cu. cm water; tube length = 10 cm; mol. = 365.5)

Wave-length Å	Rotation observed, α	Specific Rotation, $[\alpha]$	Molecular Rotation, $[M].10^{-2}$
7002	+ 1.74	+ 435	+ 1590
6737	+ 2.22	+ 555	+ 2028
6715	+ 2.23 M_1	+ 557.5	+ 2038
6494	+ 1.88	+ 470	+ 1718
6273	+ 0.66	+ 165	+ 603
6170	0	0	0
6073	− 0.56	− 140	− 512
5893	− 1.10	− 275	− 1005
5813	− 1.18 m_1	− 295	− 1078
5732	− 1.10	− 275	− 1005
5590	− 0.84	− 210	− 768
5463	− 0.42	− 105	− 384
5346	− 0.08	− 20	− 73
5300	0	0	0
5237	+ 0.10	+ 25	+ 91
5135	+ 0.18	+ 45	+ 164
5040	+ 0.28	+ 70	+ 256
4952	+ 0.32	+ 80	+ 292
4903	+ 0.33 M_2	+ 82.5	+ 301
4870	+ 0.32	+ 80	+ 292
4794	+ 0.18	+ 45	+ 164
4758	+ 0.17 m_2	+ 44.3	+ 162
4723	+ 0.18	+ 45	+ 164
4657	+ 0.44	+ 110	+ 402
4595	+ 0.48	+ 120	+ 439
4537	+ 0.52	+ 130	+ 475
4482	+ 0.70	+ 175	+ 640
4430	+ 0.92	+ 230	+ 841
4400	+ 0.94 M_3	+ 235	+ 859
4381	+ 0.92	+ 230	+ 841
4335	+ 0.76	+ 190	+ 694
4291	+ 0.56	+ 140	+ 512
4249	+ 0.28	+ 70	+ 256

TABLE XI

Rotary Dispersion of Violeo-$\left\{\begin{matrix}(Co^{III}(l\text{-Cptdin})_2)\\ Cl_2\end{matrix}\right\}Cl$

(Solution of 0.4 gm. of salt in 100 cu. cm.; tube length = 10 cm.; mol. wt. = 365.5)

Wave-length Å	Rotation observed, α	Specific rotation, $[\alpha]$	Molecular rotation, $[M].10^{-2}$
7002	+ 0.88	+ 220	+ 804
6737	+ 1.14	+ 285	+ 1042
6494	+ 1.36	+ 340	+ 1243
6400	+ 1.38 *M*	+ 345	+ 1261
6273	+ 1.36	+ 340	+ 1243
6073	+ 1.28	+ 320	+ 1169
5863	+ 1.14	+ 285	+ 1042
5732	+ 1.04	+ 260	+ 950
5590	+ 1.00	+ 250	+ 914
5463	+ 1.00	+ 250	+ 914
5346	+ 0.98	+ 245	+ 895
5237	+ 0.80	+ 200	+ 731
5135	+ 0.78	+ 195	+ 713
5040	+ 0.78	+ 195	+ 713
4952	+ 0.72	+ 180	+ 658
4870	+ 0.72	+ 180	+ 658
4794	+ 0.66	+ 165	+ 603
4723	+ 0.62	+ 155	+ 566
4657	+ 0.61 *m*	+ 152.5	+ 557
4595	+ 0.62	+ 155	+ 566
4537	+ 0.84	+ 210	+ 768
4482	+ 0.86	+ 215	+ 786
4430	+ 0.87	+ 217.5	+ 795
4381	+ 0.96	+ 240	+ 877
4335	+ 0.98	+ 245	+ 895
4291	+ 1.44	+ 360	+ 1316
4249	+ 1.46	+ 365	+ 1334
4209	+ 1.48	+ 370	+ 1352

When one tries to introduce a molecule of the *levo-* or *dextro*-rotary base into the praseo-salts of the types $\left\{\begin{matrix}Co^{III}(d)_2\\Cl_2\end{matrix}\right\}X$ and $\left\{\begin{matrix}Co^{III}(l)_2\\Cl_2\end{matrix}\right\}X$, with the object of securing salts of the types $\left\{\begin{matrix}Co^{III}\ (d)_2\\l\end{matrix}\right\}X$ or $\left\{\begin{matrix}Co^{III}(l)_2\\d\end{matrix}\right\}X$, respectively, it appears that the products desired are not formed. The expected combinations seem to be unstable from stereometric causes, and we obtain in each case only a mixture of one molecule of an active salt containing three identical molecules of the base in its cation, together with one molecule of the racemic compound, according to the reaction scheme:

$$3[ddl]^{\cdots} = 2[ddd]^{\cdots} + [lll]^{\cdots} = [ddd] + \text{racemoid.}$$

In this case also it is evident that the formation of the cation of the highest possible symmetry is favored at the cost of the complexes of lower symmetry.

In the preceding case one molecule of ethylenediamine was made to react under the most varied circumstances of temperature, concentration and difference in solvents. It soon became clear that the salts of the desired type were not sufficiently stable to permit of being obtained from solution, in each case a reaction occurred of the form:

$$3\left\{\begin{matrix}Co^{III}(Cptdin)_2\\(Ene)\end{matrix}\right\}X_3 = 2\left\{Co^{III}(Cptdin)_3\right\}X_3 + \left\{Co^{III}(Ene)_3\right\}X_3.$$

Some of our experiments—for example, our attempts to split the reaction product into two optically-active components—suggested that salts of the type desired were really formed as intermediate products; on recrystallizing the impure mass from solution, however, we never obtained anything other than a mixture of the complex salts last mentioned. In this case the components were identified by precipitating them as iodides and by precise studies of their crystal forms.

Here again the matter of transformation is quite analogous to that observed in the previous transformation of the cobaltic salts of the cation type $\left\{\begin{matrix}Co^{III}(d)_2\\ l\end{matrix}\right\}^{\cdots}$. In both cases it was always that type of ion having the lower degree of symmetry (a single, polar binary axis) that was replaced by a mixture of two kinds of cations, both of which possess a much higher symmetry $(D)_3$. On a former occasion I drew attention to the special tendency to form such complexes of a higher degree of symmetry.[1] The facts stated here give a convincing confirmation of the views on this subject stated at that time. In this case also it is the significance of the maximum symmetry in questions of relative stability of such spatial arrangements, that reduces the number of theoretically possible isomers of such complexes to the extent that we have observed here.

The experiments with salts of the type $\left\{\begin{matrix}Co^{III}(Ene)_2\\ Cl_2\end{matrix}\right\}Cl$ clearly prove, however, that a molecule of an optically active base, such as *levo*-rotary cyclopentylenediamine, may be as well introduced into a *dextro-* as into a *levo*-rotary configuration of a cation which already contains two molecules of ethylenediamine. Such an introduction is impossible, however, if two molecules of the optically-active antipode of the substitute are originally present, instead of two molecules of ethylenediamine. It would appear from this, that there is a more pronounced contrast between a *d-* and an *l*-isomer of the same compound than exists between an optically-active molecule and a totally different substance, in those cases where it is attempted to introduce them all together into the same dissymmetrical spatial configuration. The previous presence of such non-related molecules appears to be a less serious hindrance to the entrance of an optically active substitute, than is the presence of similar molecules having enantiomorphous arrangements. This fact reminds us strongly of the well known, highly "specific" action of optically-active ferments and enzymes on attackable substrates of enantiomorphous configurations.

[1] F. M. Jaeger, *Proc. acad. Wetensch. Amsterdam*, 29, 575-9 (1926).

CHAPTER X

Introduction of Asymmetrical Configurations

In addition to those phenomena accompanying the introduction of optically active substitutes into complex ions, I wish to discuss here other instances of a similar nature but in which the optically active base or acid introduced is itself of an asymmetrical configuration and not of such a rather symmetrical one characteristic of cyclopentylenediamine. We find a good example offered by 1,2-propanediamine,* $CH_3 . CH(NH_2) . CH_2 . NH_2$, which may be resolved, by means of tartaric acid,[1] into its optically-active antipodes, through fractional crystallization of the bitartrates. This base has been used for such purposes on several occasions; and complex salts of this type have been studied in detail, for example in the case of Co^{III} and Pt^{IV} atoms as central atoms of the complex ion.[2] In this connection we shall also discuss the remarkable cases of isomerism observed by Werner when investigating the optically active salts whose complex ions contain simultaneously ethylenediamine, *d*- or *l*-1,2-propanediamine and two nitro groups.[3] We then pass to the consideration of those remarkable cases of such complex ions as contain simultaneously mixed basic and acid substitutes.

Both in the case of the salts of trivalent cobalt and of salts of tetravalent platinum a partially asymmetrical synthesis occurs, just as took place in the case discussed above, where three optically-active molecules of cyclopentylenediamine were introduced into the complex ion.

*[The terms α-propylenediamine and 1,2-propanediamine seem to be used interchangeably. The abbreviation (Propin) is used in formulas.—Ed.]

[1] G. Baumann, *Ber.*, **28**, 1179 (1895). The melting-point of the *d*-bitartrate is 141°; the specific rotation of the base is $[\alpha]_D = -21°$.

[2] L. Tschugaeff and W. Sokoloff, *Ber.*, **40**, 3464 (1907); **42**, 57 (1909); A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[3] A. Werner, *Helv. Chim. Acta*, **1**, 5 (1918).

In the case of the cobaltic salts[1] it was found that the *dextro*-rotary complex contained three molecules of *dextro*-rotary 1,2-propanediamine; and conversely, that the *levo*-rotary complex contained three molecules of *levo*-rotary α-1,2-propanediamine. In no case were the other conceivable complex ions encountered. Here also the rotary dispersion appears to be highly abnormal: a zero rotation at 5035 Å and 6260 Å, and a maximum $[\alpha]$ of 455° at 5270 Å.

The graphic representation of the values of $[\alpha]$ in this case for various wave-lengths, *i.e.* the dispersion curve for the salt having three molecules of the *dextro*-rotary base, is shown in Figure 47 on page 144. For purposes of comparison the diagram also presents the corresponding curve for the cobalt salt having three molecules of *levo*-rotary cyclopentylenediamine. The latter salt evidently has a rotation of the same sign as the former. The "oppositely directed" rotation of the three "hidden" *dextro*-rotary 1,2-propanediamine molecules is still manifest over a short interval of wave-lengths, but only in the red part of the spectrum where the rotation due to the complex configuration is still small.

In the case of the corresponding platinum salts it was again found that the direction of rotation of the complex ion is opposite to that of the base introduced into it. Thus the salt $\{Pt^{IV}(l\text{-Propin})_3\}Cl_4 + H_2O$ showed the following rotations:

λ	$[\alpha]$
5270	+248°
5893	+180°
6563	+146°

Here also the only salts formed were those of the ions $\{Pt^{IV}(l\text{-Propin})_3\}_D^{\cdots}$ and $\{Pt^{IV}(d\text{-Propin})_3\}_L^{\cdots}$, and the racemic salt obtained by means of the racemic base gave, on splitting with tartaric acid, no other chlorides than those mentioned above. These facts also are explained as due to an "asymmetrical synthesis." Tschugaeff and

[1] They were prepared from $\left\{\begin{matrix}Co^{III}(NH_3)_5\\Cl\end{matrix}\right\}Cl_2$ or $\left\{\begin{matrix}Co^{III}(Pyrid)_4\\Cl_2\end{matrix}\right\}Cl$, by methods described by P. Pfeiffer and Th. Gassmann, *Ann.*, **346**, 64 (1906). A. Werner and R. Feenstra, *Ber.*, **39**, 1534 (1906).

Sokoloff had already observed that the introduction of *d* or *l*-1,2-propanediamine into complex ions of bivalent platinum—where no splitting of complex ions takes place—resulted in optically-active ions whose rotation was opposite to that of the base introduced. The following series of such salts was obtained:[1]

$$\left\{Pt^{II}\begin{matrix}(NH_3)_2\\(l\text{-Propin})\end{matrix}\right\}Cl_2; \quad [\alpha]_D = +25.2°$$

$$\left\{Pt^{II}\begin{matrix}(Ene)\\(l\text{-Propin})\end{matrix}\right\}Cl_2; \quad [\alpha]_D = +24.7$$

$$\left\{Pt^{II}\begin{matrix}(Trim)\\(l\text{-Propin})\end{matrix}\right\}Cl_2; \quad [\alpha]_D = +23.6$$

$$\{Pt^{II}(l\text{-Propin})_2\}Cl_2; \quad [\alpha]_D = +46.4$$

$$\{Pt^{II}(d\text{-Propin})_2\}Cl_2; \quad [\alpha]_D = +46.4$$

From these data we may conclude that the molecular rotation due to each molecule of active 1,2-propanediamine separately introduced into these platinum complexes, is $\pm 96°$. If the rotation of salts of the type $\{Pt^{IV}(l\text{-Propin})_3\}_D$···· were due to only the three molecules of the base they contain, the molecular rotation would be about $\pm 288°$; it has been found to be actually $\pm 1026°$, or about three and a half times greater. This shows that the rotation observed must be caused chiefly by the dissymmetrical configuration about the platinum atom; taking account of the fact that the three molecules of the base are *levo*-rotary, the actual molecular rotation of the dissymmetrical ion itself has been computed as about 780°. The surplus observed is probably due to the influence of the dissymmetrical arrangement upon the rotation of each molecule of the introduced base.

Determinations of the solubilities of the antipodes and the racemoid showed that the former were much more soluble than the racemoid at ordinary temperatures; therefore under usual conditions the racemoid is the stabler phase as compared with the antipodes.

[1] "Trim" = one molecule of trimethylenediamine: $NH_2.CH_2.CH_2.CH_2.NH_2$.

Werner[1] and Smirnoff obtained very remarkable results in the case of ethylenediammino-*act*-1,2-propylenediammino-dinitro-cobaltic salts of the flavo(*cis*)-type. Since α-1,2-propanediamine is an asymmetrically built compound, the CH_3 group, indicated in Figs. 57, 60, etc., by the symbol /', can be placed in the complex ions nearest to the plane of the two NO_2 groups, or as far distant as possible.

These geometrical isomers will be distinguished as α-compounds (prismatic crystals) and β-compounds (acicular habit). In both series the base may be either *dextro-* or *levo*-rotary and either complex ion may occur in enantiomorphous configurations D and L; therefore we have here a considerable number of possible optically-active isomers. The investigators mentioned succeeded in obtaining all of them, and thus gave a convincing proof of the accuracy of the octahedral formula proposed by Werner for complex ions of this coördination type. It is evident that there must be eight optically active isomers of the following constitutions:

$$\alpha\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (d\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{D}}; \qquad \text{I}^{\alpha}$$

$$\alpha\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (d\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{L}}; \qquad \text{II}^{\alpha}$$

$$\alpha\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (l\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{D}}; \qquad \text{III}^{\alpha}$$

$$\alpha\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (l\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{L}}; \qquad \text{IV}^{\alpha}$$

$$\beta\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (d\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{D}}; \qquad \text{V}^{\beta}$$

$$\beta\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (d\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{L}}; \qquad \text{VI}^{\beta}$$

$$\beta\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (l\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{D}}; \qquad \text{VII}^{\beta}$$

$$\beta\text{-}\left\{\begin{matrix}(\text{Ene}) & \text{Co}^{\text{III}}(NO_2)_2 \\ (l\text{-Propin}) & \end{matrix}\right\}\text{Br}_{\text{L}}. \qquad \text{VIII}^{\beta}$$

Here (I^{α} and IV^{α}), (II^{α} and III^{α}), (V^{β} and VIII^{β}), and (VI^{β} and VII^{β}) are pairs of antipodes, giving, if combined, *four true racemoids*. Besides these there are 8 *partial*

[1] A. Werner, *Helv. Chim. Acta*, 1, 5 (1918).

racemoids, they being, of course, also optically active: (I^{α} + II^{α}), (III^{α} + IV^{α}), (I^{α} + III^{α}), and (II^{α} + IV^{α}); (V^{β}+VI^{β}), (VII^{β}+$VIII^{\beta}$), (V^{β}+VII^{β}), and (VI^{β}+$VIII^{\beta}$).

Perhaps the α- and β-compounds can, moreover, form equimolecular combinations which, of course, also would be optically active. Werner does not mention them; but if they could be prepared—which is not at all improbable—there would be at least sixteen more optically-active com-

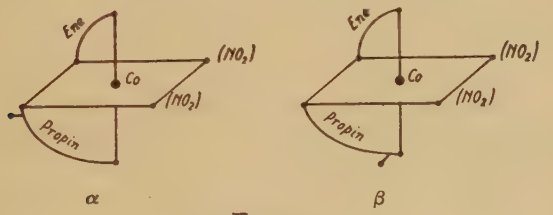


FIG. 57

pounds of a very peculiar type. Here, however, we shall restrict ourselves to those isomers that have been actually prepared. The salts to be split were obtained by starting with $\left\{\begin{matrix}Co^{III}\ (NH_3)_3\\ \quad\quad (NO_2)_3\end{matrix}\right\}$; by heating with one molecule of ethylenediamine, this was first transformed into $\left\{\begin{matrix}Co^{III}\ (NH_3)\\ \quad\quad (Ene)\\ \quad\quad (NO_2)_3\end{matrix}\right\}$, by means of *d*- and *l*-1,2-propanediamine the second compound was transformed into $\left\{\begin{matrix}Co^{III}(Ene)\\ \quad\quad (Propin)\\ \quad\quad (NO_2)_2\end{matrix}\right\}(NO_2)$, that is, into a mixture of the croceo-1,6- and flavo-1,2-nitrites. The members of this mixture can be almost completely separated from each other by adding alcohol, whereupon the croceo-salts remain in the mother liquor while the flavo-salts are precipitated. On concentrating the solution of the flavo-salts another croceo-salt is precipitated. Then the mixture of the α- and β-flavo-nitrites is transformed into the corresponding bromides, and these are resolved into α- and β-antipodes by means of silver *d*-α-bromocamphorsulphon-

ate. The separation of *d*-α-bromocamphorsulphonates of the α and β types by fractional crystallization proved a very tedious operation; but it finally gave the following results:

d-*Bromocamphorsulphonates from the racemoids with* d-*1,2-propanediamine*

1st Fr.:	II^{α}	$[\alpha]_D = +10°$;	$[\alpha]_E = +100°$.
Middle Fr.:	I^{α}	$[\alpha]_D = +60°$;	$[\alpha]_E = +30°$.
Later Fr.:	V^{β}	$[\alpha]_D = +20°$;	$[\alpha]_E = +120°$.
Last Fr.:	VI^{β}	$[\alpha]_D = 0°$;	$[\alpha]_E = +140°$.

Of these *d*-bromocamphorsulphonates the two first mentioned, and also the last mentioned pair, appeared to be derived from enantiomorphous Co^{III} complexes.

d-*Bromocamphorsulphonates from the racemoids with* l-*1,2-propanediamine*

1st Fr.:	III^{α}	$[\alpha]_D = +106°$;	$[\alpha]_E = +10°$.
Middle Fr.:	IV^{α}	$[\alpha]_D = +62°$;	$[\alpha]_E = +80°$.
6th, 7th Fr.:	$VIII^{\beta}$	$[\alpha]_D = +70°$;	$[\alpha]_E = +92°$.
8th Fr.:	VII^{β}	$[\alpha]_D = +130°$;	$[\alpha]_E = +14°$.

Of these *d*-bromocamphorsulphonates the first and the third, and similarly the second and the fourth, appeared to be derived from enantiomorphous Co^{III} complexes.

These eight *d*-bromocamphorsulphonates were then transformed into the corresponding bromides, which, after careful purification, yielded the following optically-active bromides:

II^{α}	$[\alpha]_D = -60°$	III^{α}	$[\alpha]_D = +60°$
I^{α}	$[\alpha]_D = -30°$	IV^{α}	$[\alpha]_D = +30°$
V^{β}	$[\alpha]_D = -6°$	$VIII^{\beta}$	$[\alpha]_D = +6°$
VI^{β}	$[\alpha]_D = -108°$	VII^{β}	$[\alpha]_D = +108°$

The specific rotations of the 8 partial racemoids for sodium light were:

$(II^{\alpha} + I^{\alpha})$	$[\alpha]_D = -45°$	$(II^{\alpha} + IV^{\alpha})$	$[\alpha]_D = -15°$
$(V^{\beta} + VI^{\beta})$	$[\alpha]_D = -57°$	$(I^{\alpha} + III^{\alpha})$	$[\alpha]_D = +15°$
$(III^{\alpha} + IV^{\alpha})$	$[\alpha]_D = +45°$	$(V^{\beta} + VII^{\beta})$	$[\alpha]_D = +51°$
$(VIII^{\beta} + VII^{\beta})$	$[\alpha]_D = +57°$	$(VI^{\beta} + VIII^{\beta})$	$[\alpha]_D = -51°$

Table XII

Specific Rotary Dispersions of Ethylenediammino-act-1,2-propanediammino-dinitro-cobaltic bromides

Wave-lengths Å	α-$\left\{\begin{smallmatrix}\text{(Ene)}\\(l\text{-Propin})\text{Co}^{\text{III}}(\text{NO}_2)_2\end{smallmatrix}\right\}\text{Br}_D$	α-$\left\{\begin{smallmatrix}\text{(Ene)}\\(d\text{-Propin})\text{Co}^{\text{III}}(\text{NO}_2)_2\end{smallmatrix}\right\}\text{Br}_D$	β-$\left\{\begin{smallmatrix}\text{(Ene)}\\(d\text{-Propin})\text{Co}^{\text{III}}(\text{NO}_2)_2\end{smallmatrix}\right\}\text{Br}_D$	β-$\left\{\begin{smallmatrix}\text{(Ene)}\\(l\text{-Propin})\text{Co}^{\text{III}}(\text{NO}_2)_2\end{smallmatrix}\right\}\text{Br}_D$
4920	+ 160°	− 140°	− 150°	+ 240°
4990	+ 80	− 200	− 200	0
5075	0	− 320	− 270	− 60
5170	− 30	− 320	− 320	− 112
5270	− 60	− 200	− 320	0
5300	0	—	0	—
5370	+ 72	0	+ 72	+ 200
5480	+ 240	+ 50	+ 150	+ 312
5540	+ 240	+ 100	—	—
5600	+ 160	+ 60	+ 70	+ 312
5740	+ 100	0	0	+ 192
5900	+ 60	− 30	− 6	+ 108
6075	+ 38	− 26	+ 6	+ 78
6260	+ 24	− 20	0	+ 49
6432	+ 12	− 10	0	+ 23

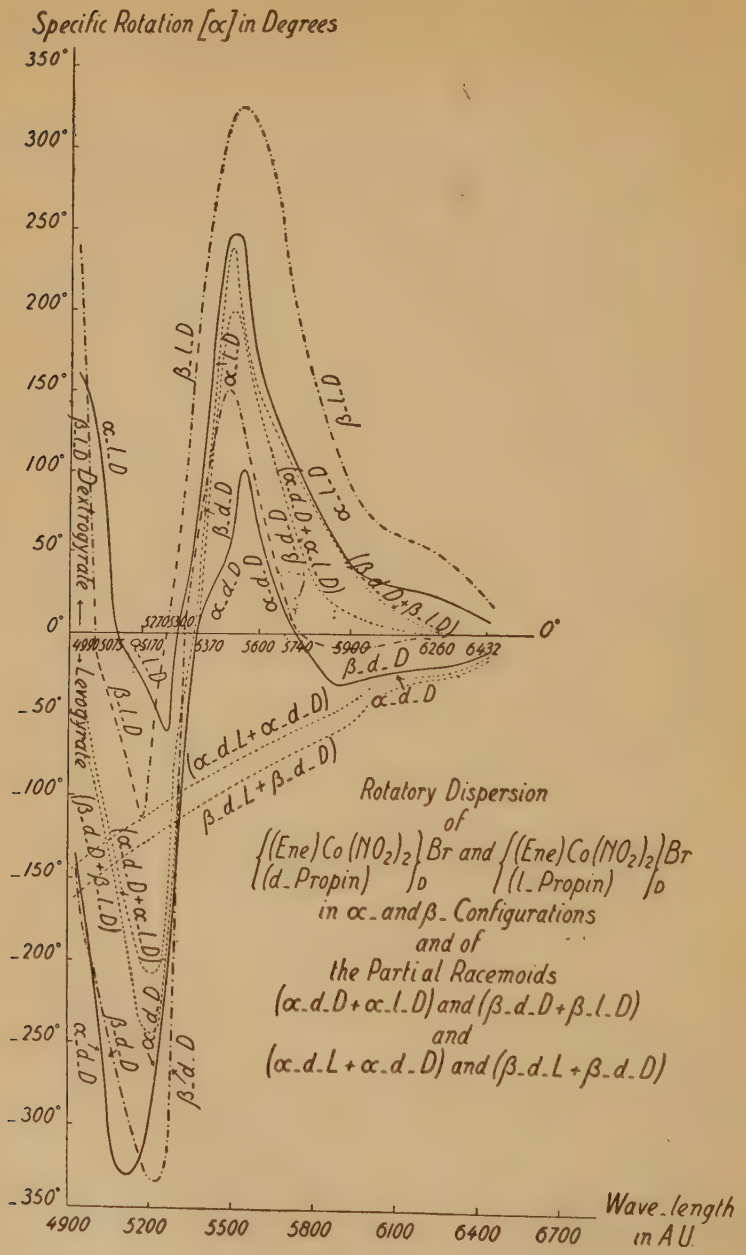

Specific Rotation [α] in Degrees
350°
300°
250°
200°
150°
100°
50°
0°
-50°
-100°
-150°
-200°
-250°
-300°
-350°
Dextrogyrate
Levogyrate
4900
5075
5170
5270
5340
5370
5600
5740
5900
6260
6432
0°
β-l-D
α-l-D
β-l-D
α-l-D
β-d-D
α-d-D
α-l-D
(α-d-D+α-l-D)
(β-d-D+β-l-D)
β-d-D
α-d-D
(α-d-L+α-d-D)
β-d-L+β-d-D)
(α-d-D+α-l-D)
(β-d-D+β-l-D)
α-d-D
β-d-D
α-l-D
Rotatory Dispersion
of
{(Ene)Co(NO2)2 (d-Propin)}Br and {(Ene)Co(NO2)2 (l-Propin)}Br
in α- and β- Configurations
and of
the Partial Racemoids
(α-d-D+α-l-D) and (β-d-D+β-l-D)
and
(α-d-L+α-d-D) and (β-d-L+β-d-D)
4900
5200
5500
5800
6100
6400
6700
Wave-length
in A.U.

FIG. 58

The rotary dispersion of most of these salts is highly abnormal, as is made plain by the data in Table XII and the corresponding curves reproduced in Figure 58. Both table and curves relate to the same, *i.e.* the right-handed, configuration (D) of the complex ion.

In the case of the partial racemoid, just as in the case of the bi[ethylenediammino]-*act.*-cyclopentylenediammino-cobaltic bromides, the dispersion is quite different from that of each of the salts.

Table XIII

Specific Rotatory Dispersion of four Partial Racemoids of Ethylenediammino-act-1,2-propanediammino-dinitro-cobaltic bromides

Wave-length Å	α-*l*D+α-*d*D (III$^{\alpha}$+I$^{\alpha}$)	β-*l*D+β-*d*D (VIIIβ+Vβ)	α-*d*L+α-*d*D (II$^{\alpha}$+I$^{\alpha}$)	β-*d*L+β-*d*D (VIβ+Vβ)
4920	− 20°	− 55°	− 144°	− 160°
4990	− 70	− 95	− 132	− 150
5075	− 130	− 160	− 123	− 140
5170	− 200	− 234	− 113	− 130
5200	− 200	—	—	—
5270	− 150	− 234	− 102	− 118
5370	0	0	− 92	− 106
5480	+ 190	+ 235	− 81	− 94
5540	+ 190	+ 235	—	—
5600	+ 120	+ 160	− 70	− 82
5740	+ 60	+ 96	− 58	− 70
5900	+ 15	+ 51	− 45	− 57
6075	+ 10	+ 38	− 34	− 42
6260	0	+ 24	− 23	− 26
6432	0	+ 10	− 12	− 14

The data of Tables XII and XIII, are presented graphically in Figure 58. With reference to this figure we may draw attention to the following features: the rotary-dispersion curves of the salts having the α as well as the β configuration are typically abnormal. They all show a steep maximum in the vicinity of 5200–5270 Å. Within this interval the salt exhibits a circular dichroïsm (Cotton effect). The curves for ions containing *l*-1,2-propanediamine are situated for the most part above the zero axis. For the

salts containing the *l*-base, the dispersion-curve of the *β*-ions is shifted to the left for shorter wave-lengths, and for greater wave-lengths to the right of the curve for the *α* ions. For the salts containing *d*-base, the zero-points of either series are almost identical (at 5370 Å.), the small shift of the *β* curve for the greater wave-lengths being in the same direction as that for the salts containing *l*-1,2-propanediamine, and for the shorter wave-lengths in the opposite direction.

The dispersion curves of the partial racemoids containing only the D-configuration of the complex—(*α*-*d*-D + *α*-*l*-D) and (*β*-*d*-D + *β*-*l*-D)—have, in both series, a shape quite analogous to those of the homogeneous active salts; they also show the Cotton effect. The curves of the partial racemoids—containing the complex ions of both D- and L-configuration—show, on the other hand, a totally different aspect. Here the dispersion apparently is normal and the Cotton effect has disappeared, evidently because of the superposition of the actions of the two mixed kinds of molecules with different dispersions. The effect of the superimposed action of two abnormally rotary molecules is here a normal rotary dispersion.

Evidently all the curves approach the zero axis in the red portion of the spectrum where the rotation of the complex ion itself is still very small, so that the influence of the rotation of the active base hidden in the complex is still preponderant.

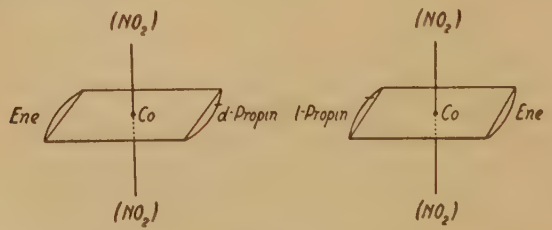


FIG. 59

Finally there have been obtained two other optically-active croceo(*trans*)-salts that are each other's antipodes (see Figure 59) and which, if combined, form a true racemoid.

The specific rotation $[\alpha]_D$ for the first ion was found to be $-10°$, and for the second ion $+10°$. In this case also, therefore, the ion containing the *d*-base is *levo*-rotary and conversely.

A case analogous to the preceding one was investigated by Hürlimann,[1] who studied the flavo-salts containing two molecules of optically-active 1,2-propanediamine;

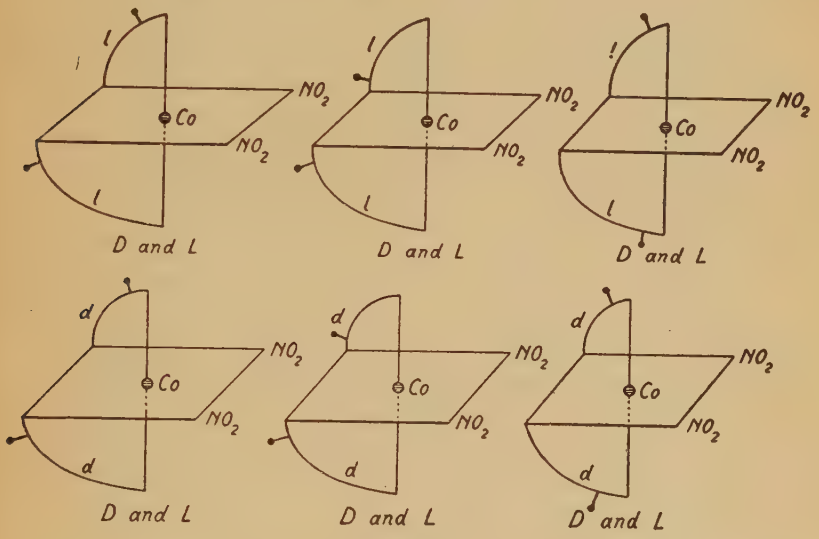


FIG. 60

some of these salts having been prepared previously by Watts.[2] Here also, when one considers the different ways of intercalation of the unsymmetrically constructed molecules of the base—as was done with the α- and β-salts of Werner—it becomes evident that we may expect, theoretically, the salts of six isomeric ions containing two molecules of the *dextro*-, and six isomeric ions with two molecules of the *levo*-rotary base (see Figure 60).

Since the ions

$\{Co^{III}(l\text{-Propin})_2(NO_2)_2\}_D^+$ and $\{Co^{III}(l\text{-Propin})_2(NO_2)_2\}_L^+$

of course are not each other's mirror images, the six racemoids of these twelve isomeric salts are themselves optically

[1] H. Hurlimann, Dissertation (Zurich, 1918).
[2] E. Watts, Dissertation (Zurich, 1912).

active in each case and are, therefore, better distinguished as partial racemoids. Moreover, there must be six true racemoids. In the course of the investigation it appeared, however, that splitting was not possible in this case. There is little doubt, therefore, that here also a "partially asymmetric synthesis" takes place if the molecules of the optically active bases be introduced into the complex ions, so that only one of its two possible enantiomorphic configurations is compatible with the presence of these active molecules. The fact that no isomerism depending on the different position of the (CH_3) group of the propanediamine molecule —as in Werner's case—was observed here, causes a further restriction in the number of isomers. The whole number of isomeric salts are thus reduced to only two and a single racemoid.

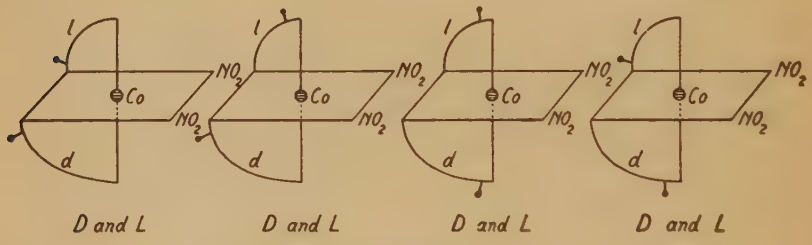


FIG. 61

The salts whose ions contain simultaneously one molecule of the *dextro-* and one molecule of the *levo*-rotary base behave otherwise. It is readily seen (Figure 61) that we may here expect the salts of eight isomeric ions.

In this case, however, the ions

$$\left\{\begin{matrix} Co^{III}\,(d\text{-Propin})\,(NO_2)_2 \\ (l\text{-Propin}) \end{matrix}\right\}_D \text{ and } \left\{\begin{matrix} Co^{III}\,(l\text{-Propin})\,(NO_2)_2 \\ (d\text{-Propin}) \end{matrix}\right\}_L .$$

are true mirror images of each other and therefore the four racemoids corresponding to these eight salts are really optically inactive. Since the *levo-* and *dextro*-rotations of the two molecules of the base also neutralize each other within each complex ion, the optical activity observed in these eight salts is only that caused by the dissymmetrical D- or L-configuration of the complex ions themselves. In a

series of investigations it was also found that there was no isomerism present due to the different possible positions of the (CH_3) groups. The number of isomers in this case is thus reduced to two and their racemoid.

TABLE XIV

Specific Rotary Dispersions of the Flavo-salts:

Wave-lengths Å	D-$\left\{\begin{matrix}Co^{III}(d\text{-Propin})(NO_2)_2\\(l\text{-Propin})\end{matrix}\right\}$Br	$\left\{Co^{III}(l\text{-Propin})(NO_2)_2\right\}$Br
	[α]	[α]
6627	+ 64.4°	+ 63.8°
6563	—	+ 71.7
6435	—	+ 71.2
6410	—	+ 70.4
6360	—	+ 66.8
6330	—	+ 71.2
6260	+ 66	+ 73.5
6075	—	+ 72.8
5985	—	+ 69.8
5895	+ 58	+ 66.8
5815	—	+ 59.1
5770	—	+ 58.7
5740	+ 39	—
5700	—	+ 52.9
5600	+ 20.4	+ 44.6
5475	+ 3	+ 22.8
5470	0	—
5370	− 26	+ 0.6
5360	—	0
5270	− 60	− 29.6
5165	− 109.1	− 123
4990	—	− 177

It was impossible to resolve the racemic salt[1] of the ion $\left\{\begin{matrix}Co^{III}\ (d\text{-Propin})\ (NO_2)_2\\(l\text{-Propin})\end{matrix}\right\}$· by means of *d*-camphorsulphonic acid or by *d*-α-nitrocamphor. The splitting of the racemoid was successfully accomplished, however, in the

[1] These salts were prepared, starting with $\left\{\begin{matrix}Co^{III}(NH_3)_3\\(NO_2)_3\end{matrix}\right\}$ in exactly the same manner as that described for Werner's flavo-salts.

case of the iodide, by treating the latter with silver *d*-α-bromocamphorsulphonate. The least soluble fraction here is that of the L-complex. The corresponding D-salts could be obtained from the mother liquor by transforming the salt into the bromide and treating this with silver *l*-α-bromocamphorsulphonate.

The brown optically active bromides crystallize in large, striated needles. For sodium light their specific

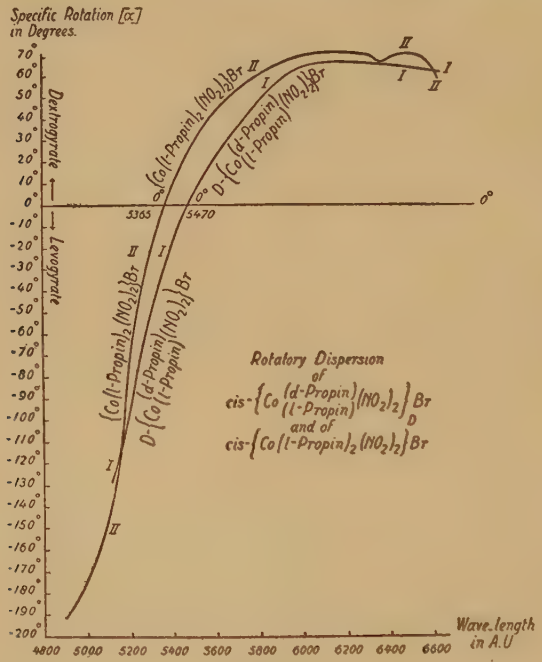


FIG. 62

rotation $[\alpha]_D$ is $\pm 58°$, and $[M]_D$ is $\pm 224°$. For the iodides these values are, respectively, $\pm 43°$ and $\pm 184°$; for the nitrates correspondingly $\pm 62°$ and $\pm 223°$; therefore the influence of the anion upon the rotation is rather considerable. Both salts seem to have highly abnormal rotary dispersion, and the same is true for the salts containing two molecules of *d*- or *l*-1,2-propanediamine. In Table XIV the values of the rotary dispersions of the flavo-salts:

$$D\text{-}\left\{\begin{matrix}Co^{III}\ (d\text{-Propin})\ (NO_2)_2\\ (l\text{-Propin})\end{matrix}\right\}Br$$

and

$$\left\{Co^{III}\ (l\text{-Propin})_2(NO_2)_2\right\}Br$$

are placed side by side, and the corresponding dispersion curves are reproduced in Figure 62.

In addition to these flavo-(*cis*)-compounds there should be also a series of corresponding croceo-(*trans*)-salts; in the case of two identical molecules (*d*- or *l*-) of the base, there must be theoretically possible here four types of complex ions which, taken pairwise, are each other's antipodes (see Figure 63).

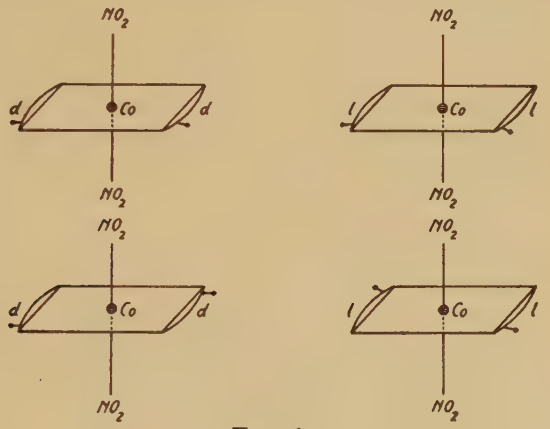


FIG. 63

We see that both kinds of salts have a binary axis of symmetry lying in, or perpendicular to, the plane of the two base molecules. The racemoids corresponding to these salts must be optically inactive. In the second case (*d*- and *l*-base simultaneously present) there can be but two kinds of isomeric ions (see Figure 64), which are not each other's mirror images, but cannot be resolved into antipodes because the first ion has a vertical plane of symmetry while the second ion has an inversion center.

In the course of the investigation it appeared that no detectable quantities of these croceo-salts were formed during the reactions. For some reason or other the action of the

optically active bases upon the trinitrotriammino-cobalt particularly favors the production of flavo-salts. This is the reason why it has not been found possible to test experimentally the above theoretical deductions.

By making $\left\{\begin{matrix}Co(Ene)_2\\Cl_2\end{matrix}\right\}Cl$ react with glycocoll, $\begin{matrix}CH_2.NH_2\\|\\COOH\end{matrix}$ in the presence of sodium carbonate, or with *N*-methylglycine (sarcosine) $HOOC.CH_2.NH(CH_3)$ in the presence of sodium hydroxide, it was possible for Meisenheimer and his collaborators to introduce these amino acids into the complex ion (Fig. 65).[1]

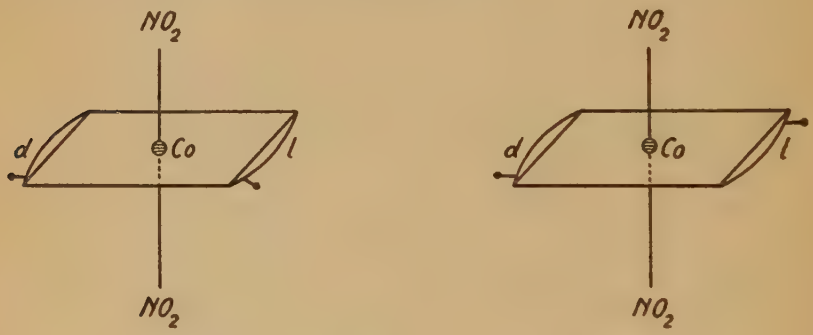


FIG. 64

Both the compounds were resolved by means of *d*-α-bromocamphorsulphonic acid. In the case of the glycocoll compounds, the salt of the *levo*-rotary ion was the least soluble product; and in the case of the iodide it was found that $[\alpha]_C = -108.5°$, $[M]_C = -544°$. An interesting result was obtained in the case of the sarcosine compound. The bromocamphorsulphonate in a 65-per-cent alcoholic solution yielded a less soluble fraction, crystallizing with 4 mol. H_2O and 2 mol. alcohol and showing $[M]_D = -920°$; and a more soluble bromocamphorsulphonate, crystallizing with 2.5 mol. of water and 1 molecule of alcohol, showing $[M]_D = +2020°$. In both cases the molecular rotations of the free ion were $-1470°$ and $+1470°$, respectively; thus there is no doubt that they are antipodes

[1] J. Meisenheimer, L. Angermann and H. Holstein, *Ann.*, 438, 261 (1924).

of each other with respect to the cobalt complex. If one recrystallizes the bromocamphorsulphonate having $[M]_D = +2020°$, the resulting crystalline product ($+4H_2O$) shows $[M]_D = +2290°$ if examined at once with a polarimeter; but within twenty-four hours this high value decreases to its normal value of $+2020°$.

There was separated off from the mother liquor another fraction, which on immediate examination showed a value of $[M]_D$ lower than the normal. This low value increased rapidly until it reached the normal value of 2020°. The reason for this can be only that the nitrogen atom of sarcosine, being co-ordinatively tetravalent and linked to (CH_3), H, (CH_2), and one of the co-ordination places, acts temporarily as a *dextro-* or *levo*-rotary substitute, but is evidently subject to very rapid autoracemization. The compound derived from the ion $\{Co^+ - N^+\}$ is evidently the bromocamphorsulphonate, having $[M]_D = 2290°$. This compound is rapidly transformed into the partial racemoid derived from $\{Co^+ - N^\pm\}$. Of the four theoretically possible isomers, one was obtained in a pure state as bromocamphorsulphonate, and the evanescent rotation of two others could be stated or represented by their mutarotation; thus there can be no doubt that the phenomenon has been correctly explained.[1]

A partial asymmetrical synthesis occurs also in cases where an optically active substitute is introduced into a resolvable complex of the kind discussed in several places above. During an investigation carried out in my laboratory by I. Lifschitz, several cases of this kind were found occurring in so-called "internal complex salts" of *d-*

[1] Attention may be drawn here to the value of mutarotation and of evanescent rotation, in general, in diagnosing the possible resolvability of rapidly autoracemizing racemoids. Compare: J. Reed and A. M. McMath, *J. Chem. Soc.*, 129, 2183 (1926); W. H. Mills and R. A. Gotts, *ibid.*, 129, 3121 (1926); H. Burgess and R. M. Lowry, *ibid.*, 125, 2081 (1924); etc. In the investigation by Mills and Gotts, here cited, the case of the optical activity of beryllium benzoyl-pyruvate,

is discussed; its brucine salt can be obtained as a derivative of the *d-*, or *l-*Be-complex. Its spirane-like structure is positively demonstrated by this fact, as in the case of basic beryllium acetate; see Bragg and Morgan, *Proc. R. Soc. London*, 104A, 437 (1923).

hydroxymethylenecamphor and *d*-nitrocamphor.[1] Such internal complex salts do not form ions; thus, in molecules such as $\{Co^{III}(Aspar.\ acid\text{-}ion)_3\}$ or $\{Co^{III}(Alanine\text{-}ion)_3\}$, the NH_2 group and the CO group are attached directly to the metallic atom.[2] In the case of the complexes of the bivalent metals Co^{II}, Ni^{II}, Cu^{II}, etc., the observed rotations were so high that they can be explained only by the dissymmetrical configuration of the complexes themselves. The highly abnormal dispersion curve, for example,

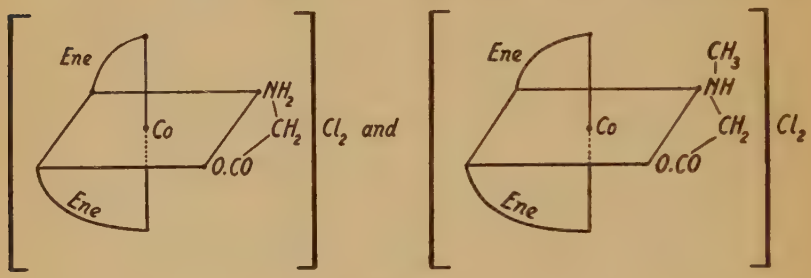


FIG. 65

of the *l*-hydroxymethylenecamphor derivative of Co^{II} measured in chloroform, and the observed Cotton effect, as well as the same phenomena in the tri-*d*-hydroxymethylenecamphor derivatives of Cr^{III} and Co^{III}, measured in alcohol, also lead to the conclusion that partial asymmetrical synthesis has taken place in all these cases. The behavior of the colorless aluminum salt is most interesting in this respect: specific rotations of not less than 2000° were observed at 4500Å. We may also consider the production of active internal complexes to be finally demonstrated for the cases of the metallic complexes of Co^{III} with *d*-alanine, where the antipodes could be isolated, and for those with *l*-aspartic acid. This is of importance since it has been proved possible to obtain, in this way, active internal complex salts which because of their constitution are stable, indifferent compounds that cannot be resolved into their optical antipodes by the usual methods. The graph repro-

[1] I. Lifschitz, *Z. physik. Chem.*, 105, 27 (1923); 114, 485 (1925); *Rec. trav. chim.*, (4) 41, 13 (1922).

[2] H. Ley and collab., *Ber.*, 42, 3894 (1909); 45, 372 (1912); 50, 1123 (1917); 57, 349 (1924).

duced in Figure 66 will give some idea of the enormous molecular rotations occurring in the complex salts of *d*-hydroxymethylenecamphor. The cobaltic salt, for in-

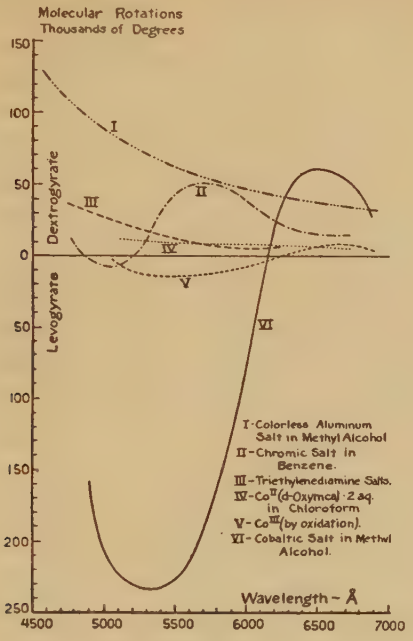


FIG. 66

stance, shows a strong rotary dispersion with circular dichroïsm, which molecular rotation amounts here to not less than $-240{,}000°$; a further conclusive proof that the magnitude of the observed rotation in such compounds is not determined by the chemical contrast between the substitutes.

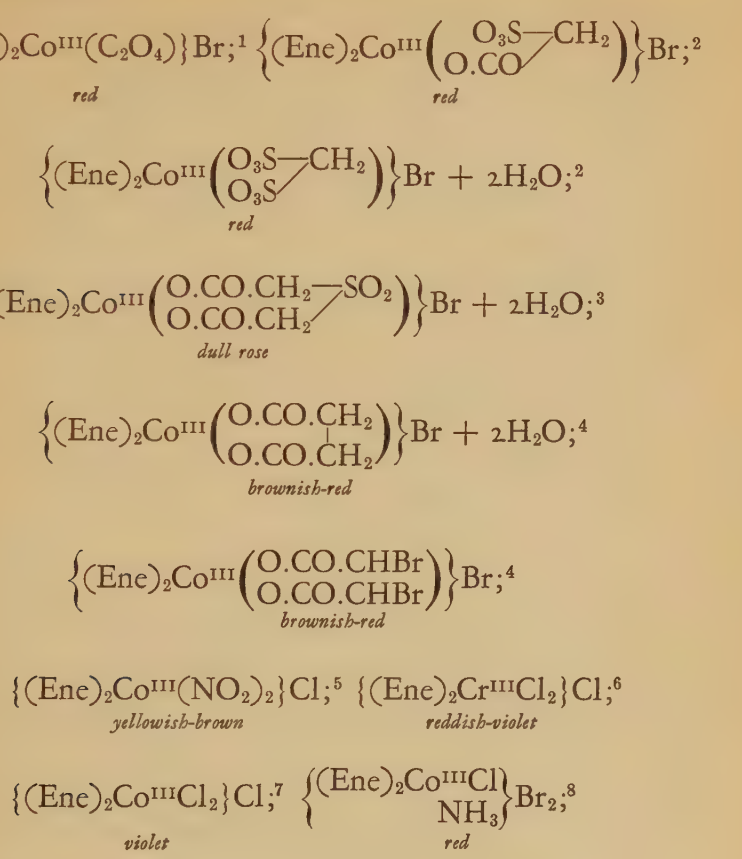
CHAPTER XI

Complex Salts with Mixed Substituents

In the preceding pages we have met, occasionally, complex salts that contain substitutes of different natures, basic or acid, in their complex ions. These kinds of complexes will now be considered more systematically, and the mutual dependence between their spatial configuration and their optical activity will be discussed. The rotatory dispersion of many of these compounds has not yet been completely investigated, and much research is still needed in this respect.

It is possible, for instance, that such complex ions contain two molecules of a bivalent pseudo-base and a third molecule of another bivalent substitute, which may be either a base or the radical of a dibasic acid. Again the ions may contain two molecules of a dibasic acid and one molecule of another dibasic acid or a bivalent base. In the third place, it may be the ion has two molecules of an univalent acid or base occupying the two co-ordination places left open by the two bivalent substitutes in the cis-position. In all these cases the symmetry of the complex ion is characterized by the presence of a binary heteropolar axis or it has no symmetry at all. In either case the complex salt will be resolvable into optical antipodes. The first successful splittings of complex salts were carried out on compounds of this very type. The influence of the introduced substitutes on the rotatory dispersion is a problem still awaiting detailed investigation. Those cases, also, where two or more central metallic atoms are present in such complex ions, are particularly of great interest in connection with the extremely high rotatory power often shown by salts of this kind.

Various types of complex salts with mixed substituents are as follows:



$\{(Ene)_2Co^{III}(C_2O_4)\}Br$;[1] *red*

$\left\{(Ene)_2Co^{III}\begin{pmatrix} O_3S & CH_2 \\ O.CO & \end{pmatrix}\right\}Br$;[2] *red*

$\left\{(Ene)_2Co^{III}\begin{pmatrix} O_3S & CH_2 \\ O_3S & \end{pmatrix}\right\}Br + 2H_2O$;[2] *red*

$\left\{(Ene)_2Co^{III}\begin{pmatrix} O.CO.CH_2 & SO_2 \\ O.CO.CH_2 & \end{pmatrix}\right\}Br + 2H_2O$;[3] *dull rose*

$\left\{(Ene)_2Co^{III}\begin{pmatrix} O.CO.CH_2 \\ O.CO.CH_2 \end{pmatrix}\right\}Br + 2H_2O$;[4] *brownish-red*

$\left\{(Ene)_2Co^{III}\begin{pmatrix} O.CO.CHBr \\ O.CO.CHBr \end{pmatrix}\right\}Br$;[4] *brownish-red*

$\{(Ene)_2Co^{III}(NO_2)_2\}Cl$;[5] *yellowish-brown* $\{(Ene)_2Cr^{III}Cl_2\}Cl$;[6] *reddish-violet*

$\{(Ene)_2Co^{III}Cl_2\}Cl$;[7] *violet* $\left\{(Ene)_2Co^{III}\begin{matrix} Cl \\ NH_3 \end{matrix}\right\}Br_2$;[8] *red*

[1] A. Werner and McCutcheon, *Ber.*, **45**, 3281 (1912); **47**, 2171 (1914).

[2] T. Slater Price and J. C. Duff, *J. Chem. Soc.*, **117**, 1071 (1920).

[3] J. C. Duff, *J. Chem. Soc.*, **107**, 367 (1915).

[4] J. C. Duff, *ibid.*, **119**, 1982 (1921). In addition to the salts already mentioned, analogous compounds were prepared with *cis*-sulphonyldiacetic acid (T. Slater Price and S. A. Brazier, *J. Chem. Soc.*, **107**, 1367, 1713 (1915)); with maleic acid, mesotartaric acid, itaconic and citraconic acids, phthalic and homophthalic acids, benzylsulphoacetic acid, *o*-sulphobenzoic acid, and bromobenzene-3,4-disulphonic acid. Most of these salts have not yet been studied with regard to their resolvability into optical antipodes. Tartaric, malic, and measconic acids did not give well-crystallized products; glutaric acid cannot be used at all for this purpose.

[5] A. Werner, *Ber.*, **44**, 2445 (1911).

[6] A. Werner, *idem*, p. 3132.

[7] A. Werner, *idem*, p. 3279.

[8] A. Werner, *idem*, p. 1887.

$$\left\{\begin{matrix}(\text{Ene})_2\text{Co}^{\text{III}}\text{Br}\\(\text{NH}_3)\end{matrix}\right\}\text{Br}_2;^{1}\ \underset{\textit{dark reddish-violet}}{}\qquad \left\{\begin{matrix}(\text{Ene})_2\text{Co}^{\text{III}}\text{Cl}\\(\text{NO}_2)\end{matrix}\right\}\text{Cl};^{2}\ \underset{\textit{red}}{}$$

$$\left\{\begin{matrix}(\text{Ene})_2\text{Co}^{\text{III}}(\text{H}_2\text{O})\\(\text{NO}_2)\end{matrix}\right\}\text{Cl}_2;^{2}\ \underset{\textit{yellow}}{}\qquad \left\{\begin{matrix}(\text{Ene})_2\text{Co}^{\text{III}}(\text{SCN})\\(\text{NO}_2)\end{matrix}\right\}\text{Cl};^{2}\ \underset{\textit{reddish-violet}}{}$$

$$\{(\text{Ene})_2\text{Co}^{\text{III}}(\text{CO}_3)\}\text{Br};^{2}\qquad \left\{\begin{matrix}(\text{C}_2\text{O}_4)_2\text{Ru}^{\text{IV}}(\text{NO})\\(\text{C}_5\text{H}_5\text{N})\end{matrix}\right\}\text{K} + 4\text{H}_2\text{O};^{3}\ \underset{\textit{red}}{}$$

$$\underset{\textit{colorless}}{\{(\text{Ene})_2\text{Ir}^{\text{III}}(\text{NO}_2)_2\}}(\text{NO}_3);^{4}\qquad \underset{\textit{brown}}{\{(\text{Propin}^*)_2\text{Co}^{\text{III}}(\text{NO}_2)_2\}}\text{Br};^{5}$$

$$\underset{\textit{brown}}{\left\{\begin{matrix}(d\text{-Propin})\text{Co}^{\text{III}}(\text{NO}_2)_2\\(l\text{-Propin})\end{matrix}\right\}}\text{Br};^{6}$$

$$\underset{\textit{red}}{\{(\text{C}_5\text{H}_7\text{O}_2)\text{Co}^{\text{III}}(\text{Ene})_2\}}\text{Br}_2 + \text{H}_2\text{O};^{6}$$

$$\underset{\textit{dark violet}}{\{(\text{C}_7\text{H}_6\text{NO}_2)\text{Co}^{\text{III}}(\text{Ene})_2\}}\text{Br}_2;^{6}$$

* Here and in the following formulas (Propin) stands for α-1,2-propanediamine.

Besides salts of the type mentioned above, salts derived from complex ions of the type $\left\{\begin{matrix}\text{A}\\\text{B}\end{matrix}\right\}\text{Me}\left\{\begin{matrix}\text{C}_2\\\text{D}_2\end{matrix}\right\}$ must be resolvable into their optical antipodes, if C_2 and D_2 are not situated in the same principal section of the octahedral configuration of the ion; and the same must hold for the type $\left\{\begin{matrix}\text{A}_3\text{Me}\ \text{B}\\\text{C}\\\text{D}\end{matrix}\right\}$ when the substitutes B, C and D are situated in the three corners of the same face of the octahedron representing the spatial arrangement of the groups in the complex. It is, for instance, easily seen that ions of

[1] A. Werner, *Ber.*, 44, 1887 (1911).
[2] A. Werner, *idem*, 3272.
[3] R. Charonnat, *Compt. rend.*, 178, 1423 (1924).
[4] A. Werner and A. P. Smirnoff, *Helv. Chim. Acta*, 3, 472 (1920).
[5] H. Hürlimann, Dissertation (Zurich, 1918).
[6] A. Werner and S. Matissen, *Helv. Chim. Acta*, 1, 78 (1918). Acetylacetone is equal to $(\text{C}_5\text{H}_7\text{O}_2)$ and benzohydroxamic acid is equal to $(\text{C}_7\text{H}_6\text{NO}_2)$. These derivatives were not resolved into their optical antipodes.

the latter kind are not superposable on their mirror images—as in both cases considered they are altogether asymmetrical (see Figure 67).

Of course AAA may be the completely equivalent radicals of one and the same molecule, and also CC or DD; as for example, the two NH_2 groups in ethylenediamine, or the two CO_2 groups in the oxalic acid ion C_2O_4''.

Werner was the first to succeed in splitting the *cis*-dinitro-di[ethylenediammino]-cobaltic chloride (1,2- or flavo-salt) by means of camphorsulphonic and α-bromocamphorsulphonic acid.[1] In using the former acid, the less

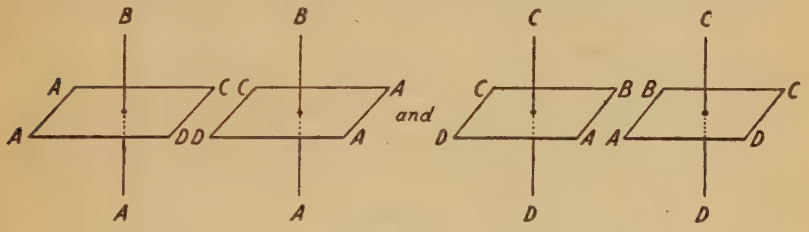


FIG. 67

soluble fraction appeared to be the *d*-camphorsulphonate of the *levo*-rotary ion; while from *d*-α-bromocamphorsulphonic acid, the salt of the *dextro*-rotary ion was the least soluble. The optically-active components show a strong highly abnormal rotary dispersion with a Cotton effect, the rotation becoming zero at a wave-length in the vicinity of the C line. Corresponding *trans*-isomers (1,6 or croceo-salts) as had been theoretically predicted, were not resolvable into optical antipodes. His solubility determinations of the flavo-salts show that the sulphate at about 28°, and the chloride at room temperature, may possibly split by spontaneous crystallization, the optically-active components in this case being less soluble than the racemoids. This fact has been overlooked hitherto and has not been tested experimentally. The specific rotation of the chloride (one-per-cent solution) appears to be about 52° for sodium light. The salts are relatively stable and their complete curves of rotary dispersion would furnish interesting objects for study.

[1] A. Reychler, *Bull. soc. chim.*, (3) 19, 121 (1898).

Less stable and subject to more rapid autoracemization, are the optically-active components of the violeo-salts:

$\{(Ene)_2Co^{III}Cl_2\}Cl$ and $\{(Ene)_2Cr^{III}Cl_2\}Cl$.

In both cases the splitting was carried out by adding the ammonium salt of α-bromocamphorsulphonic acid to the cold concentrated solutions; when using the ammonium *d*-bromocamphorsulphonate, the salt of the *levo*-rotary complex ion was obtained directly in the pure state in both cases. In the case of the chromium salt, if the mother liquor was treated with sodium dithionate the racemic compound still present therein was precipitated and the remaining salt of the *dextro*-rotary ion could be obtained as a chloroplatinate. When the solution of the latter was treated with $AgNO_3$ the nitrate of the *dextro*-rotary component was obtained immediately. The specific rotations of the Cr and Co salts were $\pm 140°$ and $\pm 200°$, respectively. Autoracemization occurs here very rapidly, however, because chloro-aquo and even diaquo salts are here easily formed under the influence of the solvent; in both cases a 0.5-per-cent solution became completely inactive within three hours, while the bromide of the cobalt salt was totally racemized in about twenty-four hours.

From the active cobalt salts the corresponding optically active carbonato salt, $\left\{\begin{matrix} Co^{III}(Ene)_2 \\ (CO_3) \end{matrix}\right\}Br$, could be prepared by means of potassium carbonate. In this way the *dextro*-rotary violeo-salt yielded the *levo*-rotary carbonato salt, and conversely. On treating the optically active violeo-salts with sodium hydroxide or sodium nitrite, however, there were produced only the wholly inactive aquo-hydroxo, and dinitro salts respectively.

The chloro-ammino- and bromo-ammino-di[ethylene-diammino]-cobaltic bromide also can be resolved by the aid of silver *d*-α-bromocamphorsulphonate, the salts of the *dextro*-rotary ions being the least soluble ones in this case. The antipodes are relatively stable; the specific rotation for the C line being about 46.2° for the bromo-ammino salts, and 43° for the chloro-ammino salts. The optically active aquo-ammino salts may be prepared from the optic-

ally active bromo-ammino salts by treating their solution with $AgNO_3$, according to the reaction-equation:

$$\left\{\begin{matrix}(Ene)_2Co^{III}Br\\(NH_3)\end{matrix}\right\}Br_2 + 3AgNO_3 + H_2O =$$

$$3AgBr + \left\{\begin{matrix}(Ene)_2Co^{III}(H_2O)\\(NH_3)\end{matrix}\right\}(NO_3)_3$$

In the case of the chloride of the chloro-nitro-di[ethylene-diammino]-cobaltic ion, also completely asymmetrical, the resolution into optically active antipodes is best accomplished by precipitating with either ammonium *d*-α-bromo-camphorsulphonate or ammonium *d*-camphorsulphonate. In using *d*-camphorsulphonate, the salt of the *levo*-rotary ion is precipitated, but with the *d*-bromocamphorsulphonate it is the salt of the *dextro*-rotary ion that comes down first. In this way these salts are obtained directly in a nearly pure state and their purification is completed by one additional precipitation and recrystallization.

Both optical antipodes show mutarotation in their solutions; for example, the specific rotation for sodium light here increases rapidly from its initial value of about 20° up to 52°; then it remains constant while the color of the solution changes from red to yellow. Mutarotation is due to transformation of the salts into their corresponding aquo-nitro salts, as could be proved by precipitating them as iodides and analyzing. This transformation took place, however, much more slowly in solutions containing hydrochloric acid at a concentration of 50 per cent. When the optically active chloro-nitro salts are treated with sodium nitrite, the corresponding optically active dinitro compounds are obtained; the *dextro*-rotary chloro-nitro salt yielded a similarly *dextro*-rotary dinitro salt. Potassium rhodanide gave, in the same way, the much more strongly rotary nitro-isorhodanato salts; their specific rotation for sodium light is here about 84°.

The experiments for resolving the oxalato-di[ethylene-diammino]-cobaltic bromide also gave interesting phenomena. The determinations of the solubilities make it certain that the optically-active antipodes are much less soluble at 17° than is the racemic salt. This seems to re-

quire the conclusion that at room temperature it is possible for splitting to take place by spontaneous crystallization, because the optical antipodes evidently are the more stable solid phases as compared with the racemoid. The antipodes are very stable indeed. Werner found that they could be prepared in a perfectly pure state, from the racemoid, by precipitation on adding alcohol to the solution provided a germ (nucleus), or a slight quantity of one of the antipodes, is added in advance. In particular it was found that under these conditions there is precipitated only that antipode which had been added previously to the inactive solution. From the resulting mother liquor the other antipode could be precipitated by the further addition of alcohol and ether. The same phenomenon was observed in the case of the dinitro-di[ethylenediammino]-cobaltic chloride.

Still more remarkable was the fact, here met for the first time, that in order to produce this selective precipitation of one of the antipodes, it is not even necessary to add one of the antipodes themselves; the result can be accomplished simply by adding the optically-active antipode of another analogously built isomorphous salt. For example, the corresponding racemic oxalato-di[ethylenediammino]-chromic salt, which could be resolved in no other way, could be split into its antipodes after precipitating with alcohol and adding to its solution a few crystals of the corresponding antipodes of the oxalato-di[ethylenediammino]-cobaltic salts mentioned above. The rotary dispersion of these antipodes is considerable in both cases: for the cobalt salt, $[\alpha]_C = 308°$ and $[\alpha]_D = 848°$; for the chromium salt the corresponding values are 164° and 332°. Since the precipitation carried out in this manner can be successful only through a range of temperatures over which the optical antipodes are more stable than the racemoid,[1] it must be concluded that in the case of the chromium salt, also, the solubility of the antipodes is less at 17° than is that of the racemic compound. This has not been tested experimentally as yet, nor has it been determined whether splitting by spontaneous crystallization may occur here. It

[1] F. M. Jaeger, *Principle of Symmetry*, p. 214f. (2d edit., 1920).

is highly desirable to carry out more systematic investigations into the special relations prevailing in such cases, because many problems in this connection remain to be elucidated.

Charonnat[1] succeeded in separating the ruthenium salt $\left\{\begin{matrix}Ru^{IV}(C_2O_4)_2\\(NO)\\(C_5H_5N)\end{matrix}\right\}K + 4H_2O$, obtained by the action of potassium oxalate and pyridine (red, triclinic crystals) on $\left\{\begin{matrix}Ru^{IV}Cl_5\\(NO)\end{matrix}\right\}K_2$, with the aid of the corresponding pink quinine salts. The quinine salt of the *dextro*-rotary ion appears to be much less soluble than that of the *levo*-rotary ion. From the quinine salts it was possible to prepare the optically active antipodes of the ammonium salt. In a 0.5-per-cent aqueous solution these show a specific rotation of $\pm 425°$ for sodium light. The antipodes are relatively stable, but they are much more soluble than the racemoid and therefore, at ordinary temperature, they represent the metastable phases with respect to the racemic compound.

Smirnoff prepared the compound, $\{(Ene)_2Ir^{III}(NO_2)_2\}I$, and was able to resolve it into its antipodes by means of the silver salts of *d*-camphorsulphonic acid. Here the least soluble salt is that of the *dextro*-rotary ion. The specific rotations $[\alpha]$ are smaller than those of the corresponding tri[ethylenediamino] salts. For example, for the nitrate the following values were determined:

λ(Å)	$[\alpha]$
5270	41.2°
5893	27.2
6563	18

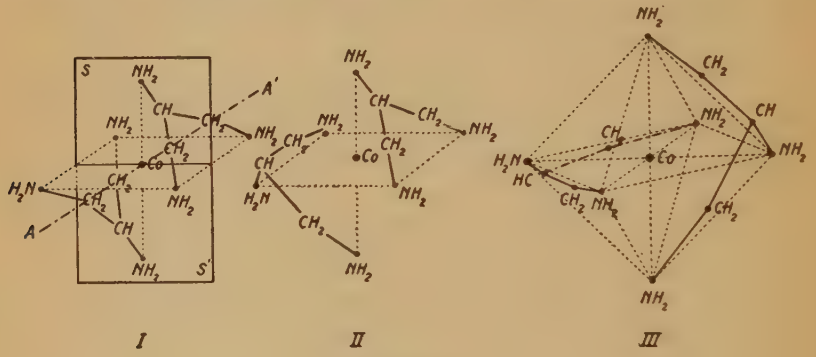
Those cases in which the substitute introduced into the complex ion is able to occupy three or four co-ordination places, are highly interesting from a theoretical point of view, and are connected in some manner with the cases just considered. Of the experiments made in this direction I will mention here only those using α,β,γ-triamino-

[1] Charonnat, *loc. cit.*

propane, $NH_2.CH_2.CH(NH_2).CH_2.NH_2$;[1] β,β',β''-triaminotriethylamine, $N(CH_2.CH_2.NH_2)_3$;[2] and with ethylenediamino-bis-acetylacetone,

$C_{12}H_{20}O_2N_2 = CH_3.CO.CH_2.C(CH_3)N.CH_2.CH_2.N - C(CH_3).CH_2.CO.CH_3$.[3]

Triaminopropane is a trivalent pseudo-base, but it can occupy two or three co-ordination places in the complex ion; moreover in the first case there is still a possibility that linkage to the central metallic atom occurs through the



I II III

FIG. 68

NH_2 groups in α,β-, or α,γ-positions. β,β',β''-Triaminotriethylamine can, co-ordinatively, be tri- or tetravalent. Ethylene-diamino-bis-acetylacetone is co-ordinatively tetravalent, both oxygen atoms of the CO groups and both nitrogen atoms exhibiting their residual affinities in the linkage to the central metallic atom. In this way a number of cases of isomerism are possible, and they will be discussed here since experiment has fully verified these theoretical deductions from the principles of tridimensional symmetry.

Mann and Pope showed[4] that triaminopropane can yield salts of Co^{III} and Rh^{III} derived from the hexammino-

[1] W. J. Pope and F. G. Mann, *Proc. Roy. Soc. London*, **109A**, 444 (1925); *J. Chem. Soc.*, **482**, 2675 (1926); F. G. Mann, *J. Chem. Soc.*, **482**, 2681 (1926); *ibidem*, p. 1224 (1927).

[2] F. G. Mann and W. J. Pope, *Chem. Ind.*, **44**, 834 (1925); F. M. Jaeger and P. Koets, *Proc. Acad. Sci. Amsterdam*, **29**, 59 (1926); *Z. anorg. Chem.*, **170**, 347 (1928).

[3] G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, **481**, 127, 2030 (1925); ethylenediammino-bis-acetylacetone was first prepared by A. Combes, *Compt. rend.*, **108**, 1252 (1889).

[4] F. G. Mann and W. J. Pope, *Proc. Roy. Soc. London*, **107A**, 80 (1925).

type, in which the six NH_3 molecules are replaced by two molecules of the trivalent base. Salts of this type, for example, $\{Co^{III}(NH_2 \cdot CH_2 \cdot CH(NH_2)CH_2 \cdot NH_2)_2\}Cl_3$, must be able to occur in three isomeric forms which are represented, on the basis of the octahedral configuration of these complex ions, by the schemes *I*, *II*, and *III*, of Figure 68.

Arrangement *I* has a binary axis *AA'*, a plane *SS'* perpendicular to it, and an inversion center in the cobalt atom; hence it cannot be resolved into optical antipodes, because the ion is identical with its mirror image. Configurations *II* and *III*, on the other hand, are both asymmetrical so that each of these ions should exist in a D- and an L-configuration, which are not superimposable. No such isomerism was found here; so it must be supposed that one of them—very probably *II*, the form of highest symmetry—is specially favored and in this case almost exclusively produced in the reaction. Some observations made during attempts to resolve them by the fractional crystallization of the *d*-camphorsulphonates in aqueous solutions at lower temperatures, seem to indicate that a very small quantity of the *d*-camphorsulphonate of an isomer having feeble evanescent optical activity and probably possessing the structure *III*, is mixed with the principal product *II*. The activity of this small quantity fell rapidly to zero and the final compound was always homogeneous and inactive.

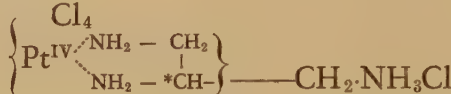
It is well known that in the neutral non-ionic salt of tetravalent platinum $\left\{\begin{matrix} Pt^{IV}(NH_3)_2 \\ Cl_4 \end{matrix}\right\}$ (see page 159) the two molecules NH_3 can be replaced by one molecule of ethylenediamine, $\left\{\begin{matrix} Pt^{IV}(Ene) \\ Cl_4 \end{matrix}\right\}$. In the same way, as has been shown by Mann,[1] one molecule of the triaminopropane can replace these two molecules of NH_3, only two of its amino groups being joined to the central platinum atom, while one NH_2 group remains uncoördinated and outside the

[1] F. G. Mann, *J. Chem. Soc.*, [129-ii], 2681 (1926); Curtius and Hesse, *J. prakt. Chem.*, **62**, 232 (1900).

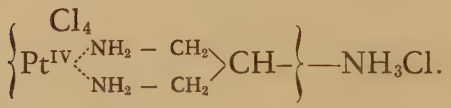
complex ion, remaining free to combine with acids into a normal salt. The resulting compound, for example, with one molecule of hydrochloric acid, is the tetrachloro-[triaminopropane-monohydrochloride]-platinum

$$\left\{\begin{matrix} Pt^{IV}Cl_4 \\ (Triprop) \end{matrix}\right\}, HCl + H_2O,$$

and it is evident that here there is the possibility of forming two isomers, since the two NH_2 groups united with the platinum atom can be the vicinal α,β ones, or the more distant α,γ ones:



or



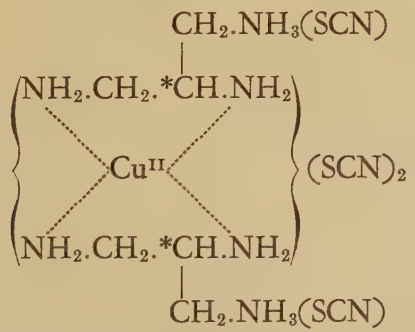
In the second case the compound cannot be resolved into optically active antipodes, because it has a binary axis and two perpendicular planes of symmetry; but in the first case the carbon atom marked * has become asymmetrical, as a result of the special manner of co-ordination, and must, therefore, occur in two enantiomorphous configurations. Experiment shows that on replacing the HCl molecule by *d*- or *l*-camphorsulphonic acid and by consecutive fractional crystallization of the camphorsulphonates at lower temperatures, one can obtain from them a *levo* and *dextro*-rotary antipode respectively, after eliminating the camphorsulphonic acid by means of $CaCl_2$. For a wavelength of 5461 Å, the molecular rotations of the antipodes were $\mp 502°$. The specific rotations $[\alpha]$ were, for $\lambda = 5780$ Å, $[\alpha] = \pm 93.2°$; and for $\lambda = 5461$ Å, $[\alpha] = \pm 108°$. The racemoid crystallizes with one molecule of H_2O, but the antipodes appear to be anhydrous. These results require one to conclude that the platinum atom is really attached to the α,β-amino groups of the trivalent base, a five-membered ring being evidently more easily formed in this case than a six-membered cycle.

The asymmetry of the β carbon atom of the base is induced only by the special mode of α,β coördination within the complex ion; hence the asymmetry does not arise until the complex compound itself is formed. This case is related, but not analogous, to Meisenheimer's case where sarcosine was introduced into a complex Co^{III} ion, discussed on page 172. In that case it was possible for the complex ion itself to assume two enantiomorphous configurations before the sarcosine was introduced; in the case under consideration this will not happen.

Mann did not succeed in replacing the chlorine atoms by ethylenediamine. Perhaps a better way to obtain a compound of the desired type would be to start with dichloro-di[ethylenediammino]-cobaltic chloride, and endeavor to introduce one molecule of triaminopropane by Meisenheimer's method. Mann was able to show also that bivalent copper can form a coördination compound with triaminopropane, of the type

$$\left\{Cu^{II}\left(\begin{matrix}NH_2.CH_2\\ |\\ NH_2.CH.CH_2.NH_3(SCN)\end{matrix}\right)_2\right\}(SCN)_2,$$

a di[triaminopropanemonothiocyanate]-cupric dithiocyanate. As the copper atom here has the coördination number 4, it is linked to only two of the NH_2 groups in each molecule of the base. By analogy with the platinum compound just considered, this copper salt very probably would have the constitution:



and the compound therefore should exist in a racemic, two optically active, and *meso* forms. If, however, the four coördination linkages of the copper atoms be directed to the

corners of a bisphenoid the complex ion would be resolvable also into D- and L-forms, unless a partially asymmetrical synthesis prohibits the production of some of these forms. The *meso* compound also would, therefore, possibly exist in two optically active forms. Experimental test of these inferences would be very interesting. Mann points out that an obstacle exists in the intensely deep violet color of these copper salts, which renders accurate

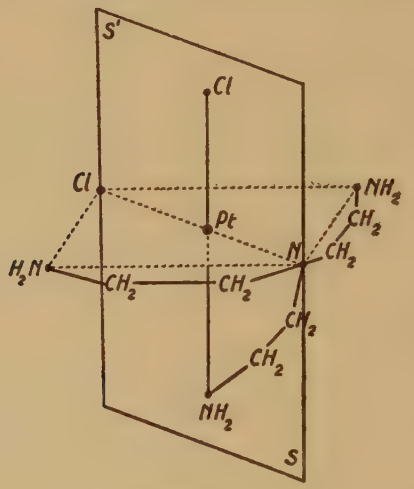


FIG. 69

polarimetric measurements rather difficult. It may be remarked that if the copper compound has a linkage with the α,γ-NH_2 groups, then no such isomerism would be possible.

Mann and Pope prepared salts of β,β',β''-triaminotriethylamine with bivalent metals, *e.g.* Ni^{II}, Pt^{II}, Pd^{II}, and with trivalent and tetravalent metals, Co^{III}, Rh^{III}, and Pt^{IV}. In the case of Co^{III}, a salt of the type

$$\{Co^{III}[N(CH_2.CH_2.NH_2)_3]_2\}Cl_3$$

was never obtained. The base appeared in co-ordination always as a tetravalent compound. Hence they prepared, for instance, dichloro-β,β',β''- triaminotriethylammino-platinic chloride, $\left\{\begin{matrix} Pt^{IV}\ Cl_2 \\ N(CH_2.CH_2NH_2)_3 \end{matrix}\right\}Cl_2$; the structure of

its ion must be that shown in Figure 69. This compound evidently has a plane of symmetry passing through both the chlorine atoms and the tertiary N atom; therefore it cannot be resolved into optically active antipodes.

We have been able to demonstrate[1] that the amine can co-ordinatively react also as a trivalent base, giving for example, through reaction with praseo-dichloro-di[ethylenediammino]-cobaltic chloride and the like, beautifully crystallized salts of nonovalent complex ions of the type:

$$\left\{\begin{matrix}&&(\text{Ene})&&\\(\text{Ene})_2\text{Co}^{\text{III}}:(\text{Triam}).&\text{Co}^{\text{III}}&.(\text{Triam}):&\text{Co}^{\text{III}}&(\text{Ene})_2\\&&(\text{Ene})&&\end{matrix}\right\}^{\text{IX}}$$

or

$$\left\{\begin{matrix}(\text{Triam})^*\\\vdots\\[\text{Co}^{\text{III}}(\text{Ene})_2]_3\\\vdots\\(\text{Triam})\end{matrix}\right\}^{\text{IX}}$$

For example, we obtained the splendidly crystallized sulphate $\left\{\begin{matrix}\text{Co}_3^{\text{III}}(\text{Ene})_6\\(\text{Triam})_2\end{matrix}\right\}_2(\text{SO}_4)_9 + 8\text{H}_2\text{O}$; the nitrate $\left\{\begin{matrix}\text{Co}_3^{\text{III}}(\text{Ene})_6\\(\text{Triam})_2\end{matrix}\right\}(\text{NO}_3)_9 + 4\text{H}_2\text{O}$; the perchlorate $(+6\text{H}_2\text{O})$; and a dithionate $(+18\text{H}_2\text{O})$. Large lustrous, hemimorphic crystals of an iodide-*d*-tartrate were also prepared.

$$\left\{\begin{matrix}\text{Co}_3^{\text{III}}(\text{Ene})_6\\(\text{Triam})_2\end{matrix}\right\}\begin{matrix}\text{I}_3\\d\text{-C}_4\text{O}_6\text{H}_4)_2\end{matrix} + 3\text{H}_2\text{O},$$

Since all our attempts to obtain optically-active components were unsuccessful, however, finally we were obliged to abandon all other suppositions concerning the structure of these ions and to assign them a configuration, in the whole series of compounds, which is probably best represented by the formula presented by Figure 70.

It is evident that an arrangement of this kind must be superposable on its mirror image and therefore cannot be resolved into enantiomorphous components.

In the case of β,β',β''-triaminotriethylamine we have already found a substitute which may eventually occupy four

[1] F. M. Jaeger and P. Koets, *Proc. Acad. Sci. Amsterdam*, **29**, 59 (1926).
*(Triam) = β,β',β''-triaminotriethylamine.

co-ordination places in the complex ion. This is much more evident in the case of the third compound mentioned above, *i.e.* the ethylenediamino-bis-acetylacetone, which in the complex ion attaches itself by means of the two oxygen and two nitrogen atoms of the substitute,

$$CH_3.CO.CH:C(CH_3):N.CH_2.CH_2.N:C(CH_3):CH.CO.CH_3,$$

because in this case it reacts in its enol form.

If the easily prepared cobaltous salt, $\{Co^{II}O_2N_2C_{12}H_{18}\}$, is oxidized by means of H_2O_2 in the presence of ammonium

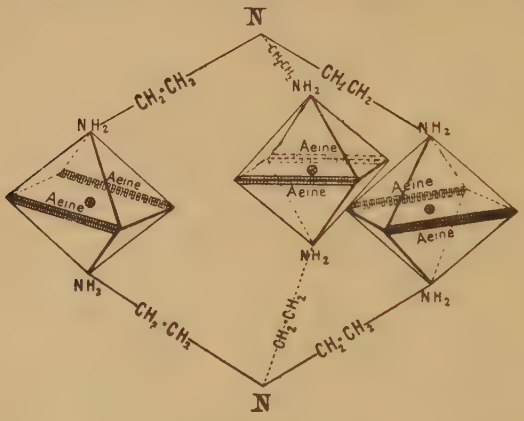


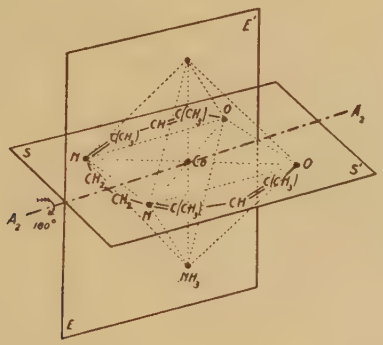
FIG. 70

chloride and a large excess of ammonia, then we obtain a complex salt of trivalent cobalt of the composition, $\left\{\begin{matrix} Co^{III}(NH_3)_2 \\ (O_2N_2C_{12}H_{18}) \end{matrix}\right\}Cl$. Since the organic substitute occupies four co-ordination places, the five isomeric configurations of the complex ion shown in Figure 71 are possible.

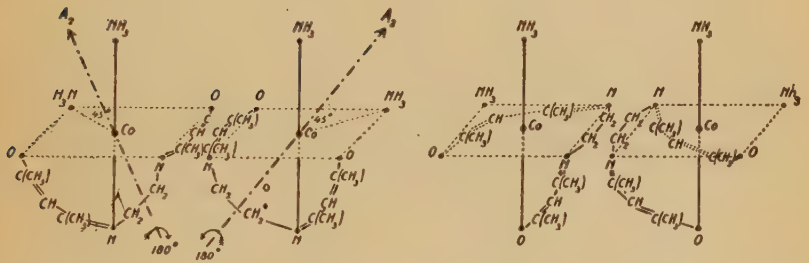
The first ion has a binary axis A_2A_2, and two perpendicular planes of symmetry intersecting in that axis; therefore this ion cannot occur in optical antipodes.[1] The second con-

[1] This conclusion by Morgan and Main Smith is not a necessary one. It is doubtful whether the nitrogen atoms that are here co-ordinatively tetravalent have their four linkages in the same principal plane of the octahedron. If they do not, there is either a single plane of symmetry passing through the two NH_3 molecules, and the compound is therefore not resolvable; or there is only a binary axis, A_2A_2, which would still permit the compound to be resolvable into antipodes. Since the latter fact has not been reported, the second seems to be the more probable configuration.

figuration, *II*, has a single symmetry-element, a heteropolar binary axis A_2 bisecting the right angle between the two NH_3 molecules; therefore it can exist in a right- and a left-handed form. The third arrangement, *III*, is totally asymmetrical, and therefore must be resolvable into optical antipodes.



I



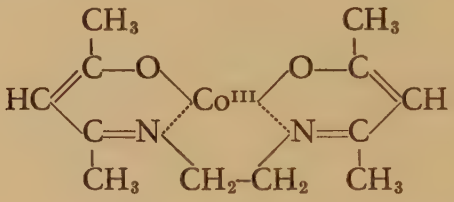
D and *L* *D* and *L*

II *III*

FIG. 71

Morgan and Main Smith converted the mixture of chlorides thus obtained, into the *d*-camphorsulphonates, which were then subjected to fractional crystallization. The first fraction was strongly *dextro*-rotary; the second fraction gave an optically-active bromide which showed a molecular rotation of 452°–531° for lithium light of a wave-length 6708 Å. Its optical activity was evanescent; its

formula probably was that of *III* of the configurations mentioned in Figure 71. The third fraction gave a bromide having $[\alpha] = 40°$, $[M]_{(6708)} = 158°$, and its formula is probably the one given as *II* in Figure 71. All optical forms were gradually transformed into the nonresolvable form *I*, and evidently this represents the most stable one. Within ten days all were converted into this form, and it then proved impossible to separate from it one of the other resolvable forms, perhaps because the laboratory atmosphere was infected with germs of *I*. The different bromides were altogether indistinguishable from one another. The authors represent the mode of linking to the cobalt atom by the following formula:



placing two six-membered and one five-membered ring within the complex ion.

In each case the deductions from the octahedral scheme here also appear to be sufficiently verified by experimental results.

CHAPTER XII

Marked Activity of Certain Complex Salts

The preceding chapter occasionally presented complex ions containing several metallic atoms. Among these compounds many separable into optically-active components appear to show very marked activity. We shall here discuss more in detail some cases of this kind.

Werner[1] prepared di[ethylenediammino]-cobaltous-μ-ammino-peroxo-di[ethylenediammino]-cobaltic salts of the general composition:

$$\left\{(\text{Ene})_2\text{Co}^{\text{III}}\begin{matrix}\text{NH}_2\\ \diagup\quad\diagdown\\ \text{O}_2\end{matrix}\text{Co}^{\text{IV}}(\text{Ene})_2\right\}\text{X}_4,$$

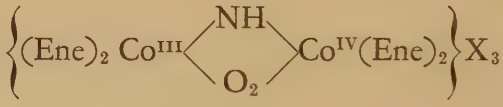
which form dark green crystals and contain a tri- and a tetravalent cobalt atom simultaneously. Since the two portions of the ion are different (Co^{III} and Co^{IV}) we may expect, theoretically, four different optically-active isomerides because both parts of the ion may have a *dextro-* or a *levo*-rotary arrangement and therefore these can occur simultaneously in the ion in four combinations:
$Co^{III}+$ and $Co^{IV}+$; $Co^{III}+$ and $Co^{IV}-$; $Co^{III}-$ and $Co^{IV}+$; $Co^{III}-$ and $Co^{IV}-$. Experience has shown, however, that only two of such combinations exist, viz., $Co^{III}+$ and $Co^{IV}+$, and $Co^{III}-$ and $Co^{IV}-$, simultaneously combined.

Starting with the tetrabromide, this compound was converted into the *d*-bromocamphorsulphonates by means of the silver salt. The precipitate of AgBr and the least soluble bromocamphorsulphonates were repeatedly extracted with hot water and the different fractions studied separately. The separation proved to be a tedious task because a brownish impurity, probably a μ-diammino salt,

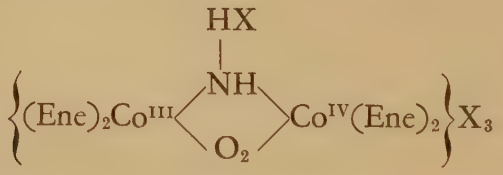
[1] A. Werner, *Ann.*, **375**, 70 (1910); *Ber.*, **47**, 1961 (1914).

was mixed with the other salts and could not be completely eliminated. It was found that the dark green *d*-camphorsulphonate of the *dextro*-rotary ion was the most soluble and the olive green *d*-camphorsulphonate of the *levo*-rotary ion the least soluble. The bromides separated from them proved to have enormous rotations: $[\alpha]$ being about 840°, and [M] therefore being about 6855° (white light). The rotary dispersion was abnormal and very large, thus $[\alpha]_D = 815°$ and $[\alpha]_E = 1200°$. Although the salts are rather stable, the optical activity decreases gradually and had completely vanished after some weeks. The enormous rotation observed depends chiefly on the presence of the tetravalent cobalt atom; if this be reduced to Co^{III}, the specific rotation of the new derivative is considerably less than before.

If NH_3 is allowed to react with the optically active salts, we obtain the corresponding dark brown imino salts



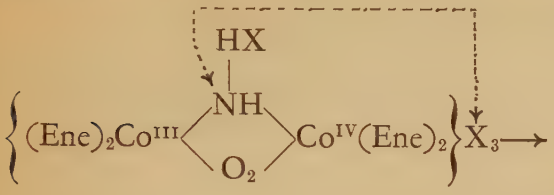
in optically-active forms.[1] In this way one obtains from the *dextro*-rotary antipode, the *levo*-rotary imino salt having $[\alpha] = -160°$. Using acids, one may also obtain in optically active forms the pale red μ-ammonium-peroxo salts:

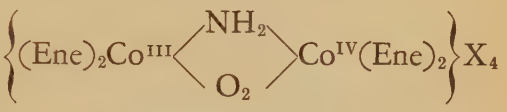


and here also the *levo*-rotary μ-ammonium-peroxo salt is obtained from the *dextro*-rotary salt, but the rotation is somewhat greater, $[\alpha]$ being here $-208°$.

[1] In these formulas (NH) takes two positive charges from the metallic atom; (NH_2) takes one; (O_2) and (SO_4) take two each; (OH) takes one; (NO_2) takes one, and so on. See A. Werner, *Neuere Anschauungen Anorganische Chemie*, p. 288–300 (Braunschweig, 1913).

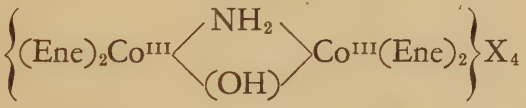
It is a remarkable fact that by simply removing X from the complex, thus making it an ion on transforming the red salt into the dark green μ-ammino-peroxo salt,



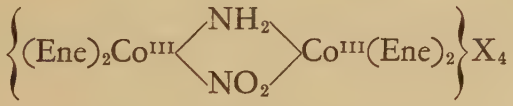


one produces a change in the molecular rotation of the ion of not less than about 8400°.

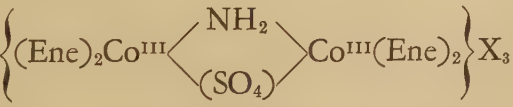
Reduction will change the original salt into the corresponding bluish-red μ-ammino-ol-dicobaltic salts,



and again the *levo*-rotary product comes from the *dextro*-rotary salt, $[\alpha]$ being here very appreciably less (110°) due to the disappearance of the tetravalent cobalt atom. With nitrous acid the dark red μ-ammino-nitro salt



is obtained in the same way; and once more the *levo*-rotary product comes from the *dextro*-rotary salt, with $[\alpha] = 158°$. Using gaseous SO_2 we obtained a red salt of the μ-ammino-sulphato series,



and the *levo*-rotary salt is derived from the *dextro*-rotary one, $[\alpha]$ now being 200°.

Interesting results were obtained on resolving tetra[ethylenediammino]-μ-ammino-nitro-dicobaltic tetrabromide,

$$\left\{(\text{Ene})_2\text{Co}^{\text{III}}\begin{matrix}\text{NH}_2\\ \text{NH}_2\end{matrix}\text{Co}^{\text{III}}(\text{Ene})_2\right\}\text{Br}_4$$

by means of bromocamphorsulphonic acid. Here fractional crystallization yielded a *dextro-* and a *levo-*rotary com-

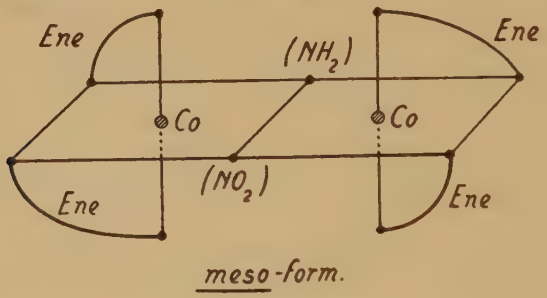


FIG. 72

pound which gave a true racemoid if the parts were combined in equimolecular quantities. There is also present here an optically-inactive isomeride that cannot be resolved into antipodes and therefore must be considered

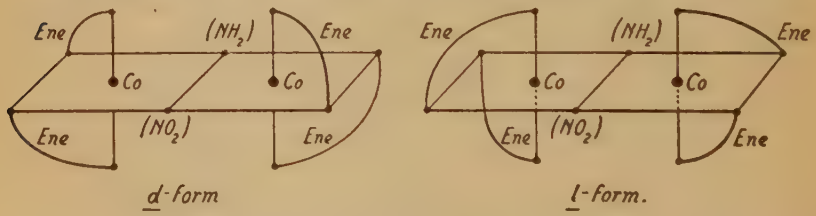


FIG. 73

analogous to mesotartaric acid. Just as the aqueous solutions of the tartaric acids when heated to 200° give the unresolvable mesotartaric acid, so the optical antipodes of this complex salt give the unresolvable *meso* form on evaporating their aqueous solutions. These facts prove that the configuration of this unresolvable salt must be symmetrical with respect to a plane, as in Figure 72;

while the optically-active components must have the configurations shown in Figure 73, having only three binary axes mutually perpendicular; and the racemoid is simply the combination, in equal quantities, of the two molecules last mentioned.

One of the most important compounds of this kind, from a theoretical point of view, is the tri[tetrammino-diol-cobaltic]-cobaltic hexachloride,

$$Co^{III}\left\{\begin{matrix}(OH)\\(OH)\end{matrix}Co^{III}(NH_3)_4\right\}_3 Cl_6$$

which was resolved by Werner into its enormously strongly rotary antipodes.[1] This case is of very great theoretical interest because the complex ion contains no carbon—thus demonstrating that the presence of carbon derivatives in such complexes is not at all a necessary condition for very strong optical activity, provided the spatial configuration of the substitutes is sufficiently dissymmetrical.

The constitution of these salts is wholly analogous to that of the tri[ethylenediammino]-cobaltic salts. Each molecule of ethylenediamine in those ions can be imagined as replaced by a group, $\left\{\begin{matrix}(OH)\\(OH)\end{matrix}Co^{III}(NH_3)_4\right\}$. The racemoid was resolved with the aid of silver *d*-bromocamphorsulphonate; the less soluble fraction here is usually the *d*-bromocamphorsulphonate of the *levo*-rotary ion. The difference in solubility of the two kinds of *d*-bromocamphorsulphonates is slight, so that the particular precipitate is determined largely by the special circumstances of the individual experiment. The optically active antipodes have a tendency to rapid autoracemization, so that their rotation is best studied in mixtures of water and acetone (a 50-per-cent mixture with the addition of some NaBr). For light of wave-length 5600 Å, $[\alpha]$ was about $-4500°$, which corresponds to a molecular rotation [M] of

[1] A. Werner, *Ber.*, 47, 3087 (1914). For its preparation see S. M. Jörgenson, *Z. anorg. Chem.*, 16, 186 (1898). The initial compound was chloro-aquo-tetrammino-cobaltic chloride, in a strong ammoniacal solution.

no less than $-47{,}610°$! The strongly abnormal rotary dispersion, accompanied by a Cotton effect, is illustrated by the following:

λ(Å)	$[\alpha]$
4780	$-86°$
4950	0
5600	$+422$
6175	0
6435	-2100

Of course these measurements are all approximate only, because of the rapid racemization; but they serve to give a good idea of the enormous rotations characteristic of this case.

While considering the remarkable compound of the preceding section, it is worth while to consider Werner's suggestion regarding the constitution of numerous basic inorganic salts, several of which occur as natural minerals.[1] He emphasizes the fact that the hydroxides of the metals also—in the absence of basic groups in complex ions—will be able to form complex salts of the tri[tetrammino-diol-cobaltic]-cobaltic type. Salts of this kind for calcium, magnesium, and zinc, would be:

$$\left[Ca\left\{\begin{matrix}OH\\OH\end{matrix}Ca(H_2O)_4\right\}_3\right]X_2;\quad \left[Ca\left\{\begin{matrix}OH\\OH\end{matrix}Ca\right\}_3\right]X_2;$$

$$\left[Mg\left\{\begin{matrix}OH\\OH\end{matrix}Mg\right\}_3\right](IO_4)_3+3H_2O;$$

Atacamite would be $\left[Cu\left\{\begin{matrix}OH\\OH\end{matrix}Cu\right\}_3\right]Cl_2$

and gerhardtite, brochantite, and langite would be the corresponding nitrate, sulphate, and hydrated sulphate ($+1H_2O$). If the two hydrogen atoms of the HO-groups be replaced by some monovalent radical R, the general formula for all these compounds is $\left[Me\left\{\begin{matrix}OR\\OR\end{matrix}Me\right\}_3\right]X_2$

[1] A. Werner, *Ber.*, 40, 44 (1907).

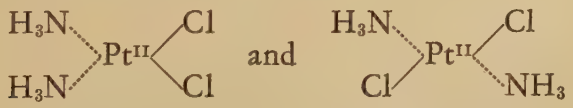
In the compounds known as "Schweinfurth greens" R is (AsO); while in the great series of the natural apatites R is (PO_3Me), (AsO_3Me) or (VO_3Me):

$$\left[Cu\begin{Bmatrix}AsO_2\\AsO_2\end{Bmatrix}Cu\right]_3(O.CO.CH_3)_2; \quad [Ca\{Ca_3(PO_4)_2\}_3]F_2; \quad [Ca\{Ca_3(VO_4)_2\}_3]F_2$$

Schweinfurth green *Apatites*

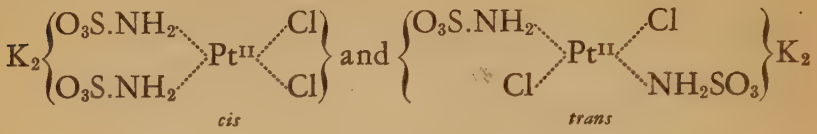
The apatites crystallize hexagonally, but have no vertical symmetry planes; this feature is undoubtedly connected with their particular architecture as expressed by the formulas above. It must be emphasized here, however, that we have no experimental proof for these formulas, in most cases, since most of the compounds are very sparely soluble and readily decomposed by chemical agents. For this reason it is not possible to demonstrate here possible optical activity in the case, for example, of the Schweinfurth greens. So far Werner's suggestion has only a theoretical value, serving as a point of departure for a general formulation of mineralogical substances in the light of the theory of the complex compounds.

While it is not desirable to go into detail here regarding the spatial configuration of complex compounds having a bivalent central metallic atom, such as Pt^{II}, Cu^{II}, it may be remarked that the problem as to whether ions with the co-ordination number 4 have a plane or a tetrahedral configuration about the central atom, is still unsolved. In a few cases it has been found possible to determine the spatial arrangement somewhat more certainly. In such a compound as a diamminoplatinous dichloride, if the four substitutes are arranged about the bivalent platinum atom in a plane we may expect two possible series of isomeric derivatives:



Indeed this isomerism of these so-called diammino-platinous and semi-diammino-platinous compounds, has

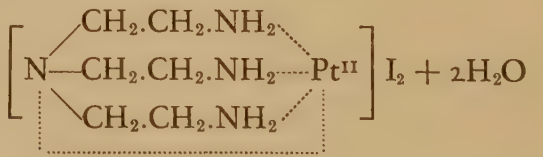
been known for a long time.[1] In other compounds having 4 as their co-ordination number, the same fact is often stated, for example, with:[2]



cis *trans*

The number of these *cis* and *trans* isomerides with compounds of this kind is very considerable. We may mention here the dipyridino-diammino-platinous, the diethylamino-diammino-platinous, and the dianilino-diammino-platinous salts.[3] Werner has concluded, from these facts, that the four co-ordination places about such atoms as Pt^{II}, Cu^{II}, Zn^{II}, Pd^{II}, and Co^{II}, are really situated in one and the same plane. Furthermore, optically-active isomerides were not observed in these cases for a long time, and all attempts to obtain them under apparently favorable circumstances seemed to be fruitless. By determining the molecular weights of *cis*- and *trans*-diammino-platinous dichloride in liquid ammonia, Reihlen and Nestle demonstrated that the *cis* compound has the normal and the *trans* compound the double molecular weight.[4] They concluded from this that this isomerism must be regarded as based on polymerism.

Reihlen emphasizes the fact that in the case of the β,β',β''-triaminotriethylammino-platinous iodide of Pope and Mann:[5]



[1] A. Werner, *Lehrbuch der Stereochemie*, p. 338 (Jena, 1904).

[2] H. Kirmreuther, *Ber.*, 44, 3115 (1911); analogous cases with Co^{II} compounds are described by Biltz and Fetkenheuer, *Z. anorg. Chem.*, 89, 121 (1914).

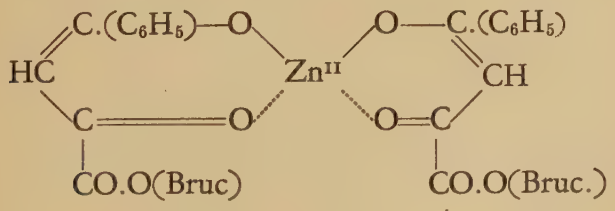
[3] A. Werner, *Lehrbuch der Stereochemie*, p. 342 (*Jena*, 1904); R. F. Weinland, *Einführung in die Chemie der Komplex-Verbindungen*, p. 185, 196, and elsewhere (Stuttgart, 1924).

[4] H. Reihlen and K. T. Nestle, *Ann.*, 447, 211 (1926); Reihlen, *ibid.*, 448, 312 (1926).

[5] F. G. Mann and W. J. Pope, *Proc. Roy. Soc. London*, 109A, 444 (1925).

and also in the corresponding di-nickel compound, the four nitrogen atoms must be distributed tetrahedrally about the central metallic atoms; the Pt^{II} compound mentioned must have a symmetry including a polar trigonal axis—on which are situated one nitrogen atom and the platinum atom—through which pass three planes of symmetry intersecting at angles of 120° (symmetry, C_3^V). Therefore this compound cannot be split into optical antipodes.

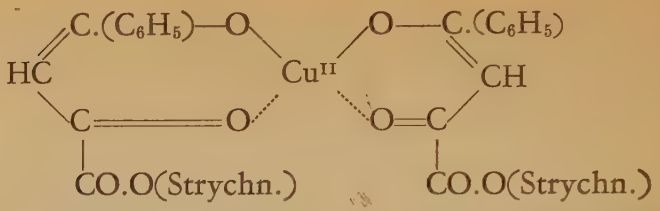
Recently, however, additional cases have been observed, so that we must conclude that under certain circumstances the four co-ordination places of the complex salts of such bivalent metals are grouped tetrahedrally about the metallic atom. As mentioned, Lifschitz, in my laboratory, observed undoubted partial asymmetrical synthesis with the internal Cu^{II} complex salts of *d*-hydroxymethylenecamphor—a fact which must be connected with the magnitude and the typically abnormal dispersion (Cotton effect) of these salts, and which is undoubtedly caused by the dissymmetrical configuration of the complex itself. Mills and Gotts,[1] as we have already learned, were able to demonstrate the existence of evanescent optically-active forms of beryllium benzoylpyruvate. Moreover, they could prove that the brucine salt of the corresponding zinc and the strychnine salt of the corresponding copper compound showed undeniable mutarotation; so that there can be little doubt that in all these salts the central metallic atom is linked to four oxygen atoms as follows:[2]



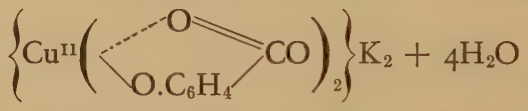
and

[1] W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, **129**, 3121, 3124f (1926).

[2] In these formulas the indicated linkages are not certain, though it can hardly be doubted that four oxygen atoms surround the metallic atom. *See also* N. V. Sidgwick, *J. Chem. Soc.*, **123**, 725 (1923).



analogous with the constitution of the corresponding beryllium salt already mentioned—a structure completely analogous with that of basic beryllium acetate, whose tetrahedral arrangement was demonstrated by X-ray analysis of its crystals. It would be worth while to investigate the possibility of such a resolution in the case of the emerald green potassium disalicylato-cupriate of Piria:



and of the corresponding salts of Ni^{II}, Co^{II}, and Pd^{II};[1] the yellow palladium salt seems to be relatively stable and well suited for such a study.

[1] G. A. Barbieri, *Chem. Zentr.*, 85 (*II*), 1102 (1914); 87(*II*), 1011 (1916).

CHAPTER XIII

Asymmetrical Photosynthesis

In preceding chapters we have met many instances of abnormal rotary dispersion, particularly circular dichroïsm in the cases of salts showing selective absorption (color) in the visible spectrum. In the present chapter I propose to discuss the possibility of effecting a totally asymmetrical photosynthesis. This is a problem that has puzzled scientists for a long time, but it has not been solved as yet. First we shall consider the significance of the problem and its scope with reference to the synthetic processes of nature.

All the innumerable processes hitherto executed in the laboratory with the purpose of preparing carbon compounds, have led to the well-known result that even when there is dis-symmetrical configuration (axially symmetrical) in the new product, the substances thus obtained never show any trace of optical activity if the reactions started with optically inactive reactants. The racemoid eventually produced in such cases may, under favorable circumstances, be resolved into its antipodes only by applying one or the other of the three splitting methods proposed by Pasteur. Starting with such optically inactive materials as are commonly employed in the laboratory, the synthetic products have always been racemic compounds or externally-compensated mixtures of the antipodes. The explanation is that in such reactions as were employed only highly symmetrical forces are active and that therefore enantiomorphic molecules have equal degrees of mechanical stability. Under such conditions there is, therefore, exactly the same chance of generating a right- or a left-handed configuration; both forms are produced at the same speed, therefore, in statistically equal numbers throughout the whole duration of the reaction. Thus the result must be always a racemoid or an externally-compensated mixture

of both kinds of molecules. The processes in the living cells of plants and animals present a striking contrast in this respect. The living plant or animal produces directly from such inactive substances as water, carbon dioxide, ammonia, formaldehyde, or hydrocyanic acid, the numberless optically-active compounds found occurring in nature. The majority of the proteids are *levo*-rotary, the bile acids are *dextro*-rotary. Plants always produce the same forms of optically-active acids and bases and carbohydrates: natural coniïne, brucine, strychnine, and other alkaloids, show always the same optical activity; the sugars formed in the cells are always only *d*-glucose and *d*-fructose;[1] and so it goes. The direct production of optically-active compounds seems, therefore, to be the very prerogative of life; and there is but an extremely small number of known cases[2] (and even some of these are pathological)[3] in which racemoids occur in the living tissues. In spite of the enormous progress in organic laboratory synthesis, there seems to exist, still, a deep and unbridgeable gulf between artificial synthesis of this kind and the natural synthetic activity occurring in the mysterious laboratory of the living cell. Pasteur was the first to put strong emphasis on this contrast and to point out that, even when we apply his second and third methods for splitting racemoids, we always make use of animal and plant products and of the physiological functions of living organisms. For him this was the most profound difference existing between other common substances and those produced under the influence of life. Plant and animal cells give rise to a strictly one-sided or asymmetrical synthesis that, as a rule, is of the most exclusive nature. A living world that is the mirror image of the one known to us, seems to be only a grotesque phantasy; the dissymmetrical specificity of it is of the highest degree.

[1] H. T. Brown and G. H. Morris, *J. Chem. Soc.*, 63, 604 (1893).

[2] K. Hess and W. Weltzien, *Ber.*, 53, 119 (1920). These workers found both forms of coniïne and methylconiïne in *Conium maculatum;* inactive atropine in *Atropa belladonna;* and the like.

[3] C. Neuberg, *Ber.*, 33, 2243 (1900). He found inactive pentose in cases of pentosuria; however, this has been criticized by I. H. Elliot, H. S. Raper, and others; *see J. Biol. Chem.*, 11, 211 (1912); H. Pringsheim, *Ber.*, 53, 1372 (1920); E. Färber, F. F. Nord, C. Neuberg, *Biochem. Z.*, 112, 313 (1920); C. Neuberg, *Ber.*, 52, 2237 (1919); and others.

Investigations of recent years have taught us, however, that striking as is the aspect of this contrast, it must be regarded as only an apparent one. Although the last and most fundamental problem here has been solved indirectly, only—and still awaits its final experimental verification—yet it must be admitted that the apparent barrier between artificial and natural synthesis has been largely removed in later years.

It becomes increasingly clear that the apparent one-sidedness of the synthesis in the living cell is only a question of relative reaction velocity in the formation of dissymmetrically constructed molecules, directed, controlled, and assisted by other optically-active substances pre-existing in them. In other words, it is the result of what we have already distinguished as "partially asymmetrical" synthetic processes.

If an optically-active compound B collaborates in a reaction by acting upon a racemoid or upon an externally compensated mixture, A_DA_L (or $A_D + A_L$)—and if the reaction be stopped at a well-chosen moment before its final complication—we shall find that unequal quantities of A_DB and A_LB will have been produced during that lapse of time. If the product be isolated and B removed from it, the substance A_DA_L (or $A_D + A_L$) thus obtained will show a positive or a negative rotation, depending on the excess of A_D or A_L present in it. The other fraction which has not yet combined with B will show, on polarimetric examination, an opposite rotation because it will naturally contain an excess of the other antipode.

We know by experience that the affinities of an optically-active substance B for either A_D or A_L are the same; but this does not by any means exclude the possibility of unequal reaction velocities, v, in the two cases. In the equations

$$B + A_D \rightleftarrows A_DB \text{ (I)}, \quad \text{and} \quad B + A_L \rightleftarrows A_LB \text{ (II)},$$

the reaction velocities are

$$v_I = k_1.C_B.C_{A_D} - k_1'.C_{A_DB} \quad \text{and} \quad v_{II} = k_2.C_BC_{A_L} - k_2'.C_{A_LB}.$$

In both cases the "affinities" are given by:

$A_I = RT.^e\ln k_1/k_1'$ and $A_{II} = RT.^e\ln k_2/k_2'$; so that if

k_1/k_1' is equal to $k_2/k_2' = K$, these affinities A_I and A_{II} will be equal, while the reaction-velocities are measured to a certain extent by $(k_1 - k_1')(k_2 - k_2')$, and all velocity-constants may, therefore, be different. This is actually the case, as the numerous investigations by Fischer,[1] Marckwald,[2] MacKenzie,[3] and others have shown. Indeed the possibility of life processes, from a chemical point of view, is at bottom a question of the mutual and dynamical regulation of reaction velocities, because the organism cannot stop its physiological function for a single moment in order to wait until "equilibrium" has been reached in these always relatively slow reactions between organic molecules. The cell produces and consumes continually; and these processes of waste and production, of metabolism and synthesis, must go on at definite, mutually well-regulated velocities if the life process is to be carried on at all. "Equilibrium" probably is never reached here; at the best there is an apparent "dynamical constancy". The antipode formed most rapidly under the dissymmetrical influences prevailing in the cell, by the collaboration of previously present optically-active reactants, is exactly that which will be most rapidly consumed in the cell's metabolism; and in the course of ages the whole physiological behavior of the organism will completely adapt itself to the use of this one antipode alone.

The particular significance of these differences in reaction-velocity for the occurrence of optically-active antipodes in living cells, has been strikingly demonstrated by the work of Dakin, Herzog and Meier, Rosenthaler[4] and of Bredig and his collaborators,[5] in their studies on the

[1] E. Fischer, *Ber.*, **32**, 3617 (1899).

[2] W. Marckwald and A. MacKenzie, *Ber.*, **33**, 208 (1900); **34**, 469 (1901); W. Marckwald, *Ber.*, **37**, 349 (1904); S. Tymstra, *ibid.*, **38**, 2165 (1905); W. Marckwald and R. Meth, *ibid.*, **38**, 801 (1905); W. Marckwald and D. M. Paul, *ibid.*, **38**, 810 (1905).

[3] A. MacKenzie, *J. Chem. Soc.*, **85**, 378, 1004, 1249 (1904); A. MacKenzie and H. B. Thompson, *J. Chem. Soc.*, **91**, 789 (1907); A. MacKenzie and H. Wren, *ibid.*, **91**, 1215 (1907); A. MacKenzie and H. A. Müller, *ibid.*, **91**, 1814 (1907); A. MacKenzie and N. Walker, *ibid.*, **121**, 350, 352 (1922); R. Weiss, *Monatsh.*, **40**, 391 (1919).

[4] L. Rosenthaler, *Arch. Pharm.*, **249**, 510 (1911); *Biochem. Z.*, **14**, 247 (1908); **19**, 186 (1909).

[5] G. Bredig and R. W. Balcom, *Ber.*, **41**, 740 (1908); G. Bredig and K. Fajans, *ibid.*, **41**, 752 (1908); G. Bredig, *Verhandl. Naturw. Ver. Karlsruhe*, **25**, —, (1913); K. Fajans, *Z. physik. Chem.*, **73**, 25 (1910); G. Bredig and P. S. Fiske, *Biochem. Z.*, **46**, 7 (1912); H. J. M. Creighton, *Z. physik. Chem.*, **81**, 543 (1913).

analogy existing between the action of ferments and enzymes on the one hand, and of optically active chemical catalysts on the other hand. Dakin, for example, found that benzyl-*l*-mandelate was decomposed by liver lipase about 40 per cent more slowly than its *dextro*-rotary isomeride. Bredig and Fajans reported that *levo*-rotary nicotine when used as a solvent—having a strongly catalytic influence on the decomposition of *d*- and *l*-camphorcarboxylic acids—decomposed the *dextro*-rotary acid into camphor and carbon dioxide more rapidly than did the *levo*-rotary acid. The decomposition velocity of the *d*-compound is here about 32 per cent greater than that of the *levo*-rotary acid. In the case of this acid and the corresponding bromocamphorcarboxylic acids studied by Fajans, the ratio of the decomposition velocities $v_D : v_L$ appeared to be 1.19 when acetophenone was the solvent and *d*- and *l*-nicotine was added in small quantities as a catalyst. When using quinine and quinidine this ratio was as high as 1.46 at 70°. These and other facts make it evident that the well-known "specificity" of enzyme action also is really of a quantitative rather than a qualitative nature, since it is based upon an appreciable difference in the decomposition velocities of the antipodes in their intermediate combinations with the dissymmetrical catalyst.

It will be clear from the foregoing that we have here no such prime barrier between the partially asymmetrical synthesis taking place in the living cells and tissues, as was supposed by Pasteur. It is in principle, only the difference in reaction speed in forming the one or the other antipode under the dissymmetrical circumstances within the cells, that causes the apparent differences between living and "dead" matter. The synthesis performed by the living organism cannot be expected even to attain the highest degree of mechanical stability, nor therefore of symmetry, because it has not time to wait for the attainment of states of perfect equilibrium, but must continually synthesize and consume at exactly regulated rates. Asymmetrical synthesis, as occurring under the influence of pre-existing optically-active and therefore guiding substances in the cell, may no longer be regarded as the prerogative of

life; although its typical one-sidedness in plant and animal cells is acquired only as the hereditary result of chemical functions developed slowly in the general course of organic evolution during unnumbered ages. The sharp line of demarcation between dead and living nature, once so clearly traced by vitalists, we may now consider to have been erased, at least in principle, forever. Although the facts of the one-sidedness of nature's syntheses have now been brought completely within the scope of our laboratory experiments, yet the great fundamental problem underlying it all has so far failed of solution.

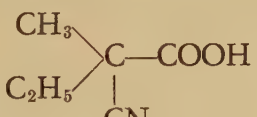
How was the first optically-active substance produced, that substance whose very presence initiated the guiding influence in the chemical synthesis of plants and therefore also of animal cells for all future time? If, in place of this one optically active substance, its antipode had been present at that initial and critical moment the whole living world would presumably have become, chemically, the complete mirror-image of the present one. It must be clear that the cause leading to the formation of that first optically-active substance out of optically-inactive materials, must be sought outside of all living matter, and therefore that it must once have acted under the influence of external and inherently dis-symmetrical forces and conditions. Hence, today the problem is to accomplish experimentally such a "totally asymmetrical" synthesis by starting with optically inactive substances and subjecting them to such external dis-symmetrical influences as are essential conditions for the reactions between them. Here great difficulty confronts us: we can indeed realize such external dissymmetrical conditions in several ways, but we must also make sure that the reaction will not take place in the absence of these conditions, and moreover that these dissymmetrical conditions actually will cause differences in reaction velocity sufficiently great to produce an observable effect in the resulting product.

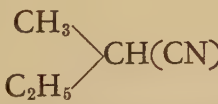
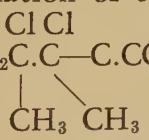
Such dissymmetrical conditions have only axially symmetrical character and are produced, for example, if a magnetic field is superimposed upon a homogeneous electrostatic field in such manner that the two sets of lines of

force are mutually parallel. Again, they result when a linearly polarized beam of light is subjected to electromagnetic torsion in a strong magnetic field which it traverses; or if right- or left-handed, circularly or elliptically polarized light is used, provided all these causes fulfill the condition of being essential for the processes taking place.

Experiments designed to influence chemical reactions by superimposing electric and magnetic fields, are not easily conceived. Hitherto all attempts in this direction have failed, either they were badly planned or—and this is the principal drawback—the presence of these external fields of force was *not* an "essential" condition for initiating the chemical process. The latter condition is much more easily met if we employ the second and third arrangements mentioned in the last section. In this case one need only to discover a suitable photochemical reaction which does not take place in the desired form except under the influence of a particular light radiation. Moreover, it must be of such a nature as to either newly create a dis-symmetry in the resulting molecule, or an existing dis-symmetrical arrangement in the molecule is attacked by the radiation in such a way that it induces unequal decomposition-velocities of the *d*- and *l*-molecules present in the original racemoid or externally compensated mixture.

As an instance of the first kind we may mention an experiment by Henle and Haakh,[1] who studied the transformation of methylethylcyanoacetic acid:



into methylethylacetonitrile:  ; and the transformation of symmetrical dichlorodimethylsuccinic acid,  , into dichlorodimethylpropionic

[1] F. Henle and A. Haakh, *Ber.*, 41, 4261 (1908).

acid, $HO_2C.\overset{Cl}{\underset{CH_3}{C}}—\overset{Cl}{\underset{CH_3}{C}}H$, both under the collaboration of the

catalytically-active uranyl salts, as influenced by linearly-polarized light traversing a magnetic field, and as influenced by *l*- and *d*-circularly-polarized light produced by $\frac{1}{4}\lambda$ mica plates. No positive result, however, was secured in these experiments.

The strongly absorbing (colored) optically-active complex salts exhibiting circular dichroïsm are particularly well suited for experiments by the second method.[1] It has already been explained that the phenomenon of circular dichroïsm is due to the unequal absorption of right- and left-handed circularly-polarized light of special wave length, by the optically active substances present in the solution. In such cases the observed "ellipticity" is a measure of the difference in absorption experienced by the right-handed and the left-handed circularly-polarized waves while passing through the solution. If this difference in absorption be sufficiently great, it is probable that the *dextro* and *levo*-rotary photochemically sensitive antipodes present in an optically-active solution will be decomposed at different speeds by light of that particular wave-length for which absorption is an optimum. After some lapse of time the solution will become slightly active and the activity will increase with the duration of the experiment.

Another way to show this would be to subject both antipodes, in separate solutions, to such a radiation and in both cases measure directly and accurately the decomposition velocities. It was this latter method that we employed for studying the photochemical decomposition of the *dextro*- and *levo*-rotary potassium trioxalato-cobaltiate $K_3\{Co^{III}(C_2O_4)_3\} + 3H_2O$ in solutions subjected to the influence of right- and left-handed circularly-polarized light. The photochemical reaction that takes place here can have its general features written as follows:

$$2K_3\{Co^{III}(C_2O_4)_3\} = 3K_2C_2O_4 + 2Co^{II}C_2O_4 + 2CO_2$$

[1] F. M. Jaeger and G. Berger, *Rec. trav. chim.*, 40, 153 (1921), and unpublished experimental results; A. Cotton, *J. chim. phys.*, 7, 81 (1909).

Cobaltous oxalate precipitates from the green solution as an insoluble rose colored powder; the potassium oxalate of this reaction combines with a small quantity of the cobaltous salt to form a complex salt having the composition $K_2\{Co^{II}(C_2O_4)_2\}$, but this compound is very strongly dissociated in solution. The absorption maxima for the emerald green solution are located at $\lambda = 4260$ Å and $\lambda =$

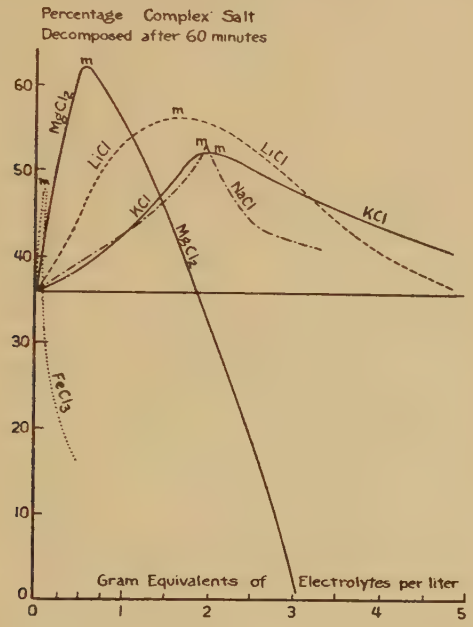


FIG. 74

6050 Å. There are here present many possible sources of error, as has been pointed out by Vránek.[1] For example, in the dark the reaction proceeds very slowly; but the influence of light-radiation, particularly in more dilute solutions, seems to be something other than a mere photocatalytic one since the temperature coefficient is very large in this case. The character of the decomposition is that of an accelerated bimolecular or of a retarded monomolecular reaction, and is of the zero order at high concentrations only. We found, moreover, that the velocity depends in a

[1] J. Vránek, *Z. Elektrochem.*, 23, 336 (1917).

marked degree on the presence of inorganic salts, this catalytic action varying with the concentration of these salts up to a certain maximum and then, on further addition of the salt, decreasing and in some cases even becoming negative (see Figure 74). The maximum effect of the added salt is reached at its lower concentrations, since the electrical charge of the cation is the higher one. This permits the reaction velocity to be regulated within certain limits. If no other salts are added, the quantity of the complex oxalate decomposed during a given time interval seems to be independent of the initial concentration (zero order) when the general concentration is high; but with smaller concentrations this character, which points to a purely photocatalytic influence, is lost.

With these solutions several measurements of the reaction-velocity were made, enabling us to study the influence of right-handed and left-handed circularly polarized light—produced from linearly polarized light by means of quarter-wave-length plates—in case of the *d*- as well as of the *l*-components. No differences in speed could be detected within the limits of experimental error.

Although in this case the result was negative, it is worth while repeating these experiments, using other complex salts of the same type and under better defined conditions. The writer is convinced that the solution of this problem must be sought in this direction.

Japp and others have previously suggested that the primitive optically-active substance that determined the special direction of all subsequent partially asymmetrical synthesis in plants and animals, was selected as the result of a splitting of a racemoid by spontaneous crystallization, one of the components having been then eliminated by some accidental mechanical influence.[1] It must be evident, however, that such a mere accidental separation of both antipodes would certainly have repeated itself many times in the course of the immeasurable periods of geological evolution; and that the collective re-

[1] F. R. Japp, *Chem. News*, 77, 139, 149 (1898); G. F. Fitzgerald, *Nature*, 58, 545 (1898); C. O. Bartrum, *Nature*, 58, 455 (1898); H. Spencer, *Nature*, 58, 592 (1898); 59, 29 (1899); K. Pearson, *Nature*, 58, 495 (1898); 59, 30, 125 (1899); G. Errera, *Nature*, 58, 616 (1898); and others.

sults of these repetitions must have led to an externally-compensated living world and not to the remarkably one-sided world that we actually know. One may ascribe greater probability to the supposition that the exclusive separation of one of the antipodes in its field of stable existence, was due to a germ of an inactive, but hemihedrally crystallizing substance, such as glycocoll, coming into contact with supersaturated solutions. Such a phenomenon was observed, as mentioned before, by Ostromisslensky.[1] If this phenomenon took place within a vegetable cell whose contained solutions were supersaturated with some organic compound resolvable by spontaneous crystallization under the prevailing conditions, it would be at least conceivable that in this way an optically-active antipode might come to be incorporated in the cell, thus determining its one-sided synthesis for all future generations. Ostromisslensky's experiments need further corroboration, however, and to be expanded over a larger number of cases, before we may regard his results as final. Until this has been done we are inclined to look for physical causes outside of the living organism, and in such a search the greater chance of discovering the correct cause is undoubtedly in the field of photochemical phenomena.

We have laid emphasis on the consideration, that during the unnumbered ages of geological evolution such a one-sided physical cause may have been always present in the form of solar photochemical energy.[2] As pointed out by Jamin,[3] sunlight reflected by the surface of the sea is always in part elliptically polarized as the result of the terrestrial magnetic field.[4] This elliptically polarized light must, then, always contain an excess of light having a particular rotation direction; and it is very probable that there has been a continuous supply, throughout the earth's history, of the necessary dissymmetrical energy. Therefore, if the wave-length of maximum light absorption by a given substance is at the same time the optimum for photochemical

[1] I. Ostromisslensky, *Ber.*, 41, 3035 (1908). The hemihedrism of glycocoll is not proved as yet; the hydrochloride, however, is rhombic bi-sphenoidal.
[2] A. Byk, *Z. physik. Chem.*, 49, 641 (1905).
[3] J. Jamin, *Compt. rend.*, 31, 696 (1850).
[4] H. Becquerel, *Compt. rend.*, 108, 997 (1899).

action,[1] the reaction velocity must surely be different from that when the antipodes are attacked by the circularly- or elliptically-polarized light of oppositely directed rotation. This would seem to require that terrestrial photochemical synthesis should be always asymmetrical; and the only problem is to discover the materials and experimental conditions suitable to demonstrate its occurrence in the laboratory.

The very latest experiment in this direction is reported by Kuhn and Braun working with K. Freudenberg.[2] These workers report that they observed an effect of about 0.10° when using *d*- or *l*-rotary circularly-polarized light of $\lambda = 2800$Å to illuminate an alcoholic solution of racemic ethyl α-bromopropionate $CH_3 \cdot CHBr \cdot CO \cdot OC_2H_5$. The algebraic sign of the observed rotation is opposite, according as *dextro*-rotary or *levo*-rotary light is used—a fact that seems to corroborate the views of the above authors that a totally asymmetrical synthesis, based on a Cotton effect in the ultra-violet, seems to have taken place. Unfortunately we have no details regarding the reaction that has taken place here, so that it is hardly possible to judge, at present, whether the effect observed is really the one looked for.

[1] J. M. Eder, *Sitzb. Akad. Wiss. Wien, Abt. IIA*, **90**, 1097 (1885); **92**, 1346 (1885); **94**, 75 (1886).

[2] W. Kuhn and E. Braun, *Naturwissenschaften*, **17**, 227 (1929).

APPENDIX

Theory and Measurement of Circular Dichroïsm

With respect to the theory and measurement of circular dichroïsm, the following additions to what has been said about it in the text may help to elucidate matters in more precise form.

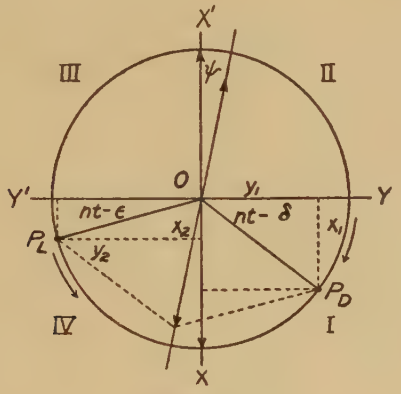


Fig. 75

1. Fresnel's explanation of optical rotation is based on the fact that two circularly-polarized, harmonic vibrations having the same period T and amplitude a, but of opposite directions of rotation, are always equivalent to a single linearly-polarized vibration with the same period T, but with a double amplitude = 2a.
Demonstration. (Co-ordinates as in Figure 75.)
Let both circular vibrations have the components:

dextro-rotary	*levo-rotary*
$x_1 = a.\sin(nt - \delta)$	$x_2 = a.\sin(nt - \epsilon)$
$y_1 = a.\cos(nt - \delta)$	$y_2 = -a.\cos(nt - \epsilon)$

δ and ϵ being phase-angles $= n.\tau_1$ and $n.\tau_2$, in which $n = 2\pi/T$.

If $(nt - \delta)$ is indicated by θ_1 and $(nt - \epsilon)$ by θ_2, the components of the resultant vibration,

$$x_s = x_1 + x_2 = a.(\sin\theta_1 + \sin\theta_2)$$
$$\text{and} \quad y_s = y_1 + y_2 = a.(\cos\theta_1 - \cos\theta_2)$$

$$\text{are} \quad x_s = 2a.\sin\left(\frac{\theta_1 + \theta_2}{2}\right)\cos\left(\frac{\theta_1 - \theta_2}{2}\right)$$
$$y_s = 2a.\sin\left(\frac{\theta_1 + \theta_2}{2}\right)\sin\left(\frac{\theta_2 - \theta_1}{2}\right)$$

From this it follows that:

$$y_s/x_s = \tan\tfrac{1}{2}(\theta_2 - \theta_1) = \tan\tfrac{1}{2}(\delta - \epsilon) \qquad 1'.$$

The variable distance OP = s being always $= \sqrt{x_s^2 + y_s^2}$, we find:

$$s = 2a.\sin\left(\frac{\theta_1 + \theta_2}{2}\right) = 2a.\sin[nt - \tfrac{1}{2}(\delta + \epsilon)] \qquad 1''.$$

The resultant vibration is, therefore, a linear one with the same period T and the double amplitude 2a. The angle ψ of this vibration with the axis OX is given by $\tan\psi = \tan\tfrac{1}{2}(\delta - \epsilon)$, according to equation 1′;

therefore $$\psi = \tfrac{1}{2}(\delta - \epsilon) \qquad 1'''.$$

If the original phases of the circular beams are δ and ϵ, the resultant linear vibration has the phase $\tfrac{1}{2}(\delta + \epsilon)$, while it makes with the X-axis an angle equal to $\tfrac{1}{2}(\delta - \epsilon)$.

1^. Conversely: A linearly-polarized vibration, having the amplitude a and the period T, can always be considered as the resultant of two oppositely directed, circular vibrations with the same period T, but half the amplitude $\tfrac{1}{2}$a.

Demonstration.

The linear vibration may be: $s = a.\sin(nt - \beta)$ $\qquad 2'.$

As we have seen in the preceeding theorem, the phases ζ and η, of the circular vibrations must fulfill the condition that $\zeta + \eta = 2\beta$; while, if ψ is the angle of the linear vibration with the X-axis, $\psi = \tfrac{1}{2}(\zeta - \eta)$.

Therefore: $\zeta = (\beta + \psi)$ and $\eta = (\beta - \psi)$.

Both the circular vibrations have, therefore, the components:

dextro-rotary	*levo-rotary*
$x_D = \frac{1}{2}a.\sin[nt - (\beta + \psi)]$	$x_L = \frac{1}{2}a.\sin[nt - (\beta - \psi)]$
$y_D = \frac{1}{2}a.\cos[nt - (\beta + \psi)]$	$y_L = -\frac{1}{2}a.\cos[nt - (\beta - \psi)]$

1[B]. Rotation of the plane of vibration of a linearly-polarized vibration in traversing an optically active medium without selective absorption.

According to Fresnel, the action of such a medium is caused by the circumstance that the speeds v_D and v_L of both opposite circular vibrations resulting from the linear one, are unequal in that medium. If the layer traversed by them has a thickness l (length of the tube in the case of a solution), the phases δ and ϵ of both rays are therefore $n.\tau_1$, and $n.\tau_2$, if $\tau_1 = l/v_D$ and $\tau_2 = l/v_L$.

So that $\delta = \frac{2\pi.l}{v_D.T}$ and $\epsilon = \frac{2\pi.l}{v_L.T}$.

If the incident vibration has the amplitude a, the components of both circular vibrations are:

dextro-rotary	*levo-rotary*
$x_D = \frac{1}{2}a.\sin(nt - \delta)$	$x_L = \frac{1}{2}a.\sin(nt - \epsilon)$
$y_D = \frac{1}{2}a.\cos(nt - \delta)$	$y_L = -\frac{1}{2}a.\cos(nt - \epsilon)$

The components of the emerging linear vibrations are:

$$x_S = x_D + x_L = a.\cos\left(\frac{\delta - \epsilon}{2}\right)\sin\left[nt - \left(\frac{\delta + \epsilon}{2}\right)\right]$$

$$y_S = y_D + y_L = a.\sin\left(\frac{\delta - \epsilon}{2}\right)\sin\left[nt - \left(\frac{\delta + \epsilon}{2}\right)\right]$$

The observed rotation ψ is given by: $\tan\psi = \frac{y_S}{x_S} = \tan\frac{1}{2}(\delta - \epsilon) = \frac{\pi.l}{T}\left(\frac{1}{v_D} - \frac{1}{v_L}\right)$, or, after introducing the refractive indices n_D and n_L of both circular rays in the solution with respect to the vacuum for that wave-length, and considering that $\lambda = v_0.T$, we find:

$$\tan\psi = \tan\tfrac{1}{2}(\delta - \epsilon) = \frac{\pi.l}{\lambda}(n_D - n_L).$$

The observed rotation is, therefore, proportional to l and equal to half the phase-difference of both circular rays, attained during their passage through that layer of the solution.

The resultant vibration $s' = \sqrt{x_s^2 + y_s^2}$ is, of course, $s' = a.\sin\left[nt - \frac{\pi.l}{\lambda}(n_D + n_L)\right]$.

If $v_D > v_L$, then $n_D < n_L$, and $\tan\psi$ is *negative* (*levo*-rotation), and *vice versa*.

2. Circular Dichroïsm.

If the solution has a strong selective absorption, it may be that in the neighborhood of some absorption bands a Cotton effect is observed, if those absorption bands correspond to groups of electrons forming part of the system of those which cause the optical activity.

The action consists in diminishing the amplitudes of the *dextro-* and *levo*-gyrate circular rays in an unequal degree, because the circular rays are unequally absorbed. When the molar absorption-coëfficients are k_D and k_L, and C is the molar concentration of the liquid, l the length of the tube, the amplitudes p and q of both circular rays, on emerging from the tube, will be:

$$p_D = \tfrac{1}{2}a.e^{-i.\frac{2\pi}{\lambda}k_D.C.l} \quad \text{and} \quad q_L = \tfrac{1}{2}a.e^{-i.\frac{2\pi}{\lambda}k_L.C.l}$$

The *dextro*-gyrate vibration will have the components:

$$x_1' = p.\sin(nt - \delta)$$
$$y_1' = p.\cos(nt - \delta)$$

and likewise the *levo*-gyrate vibration:

$$x_2' = q.\sin(nt - \epsilon)$$
$$y_2' = -q.\cos(nt - \epsilon)$$

According to a well-known theorem, both these vibrations will give a resultant of the form:[1]

[1] If the vibrations are: $s_1 = a.\sin(nt - \delta)$ and $s_2 = b.\sin(nt - \epsilon)$, then $s_1 + s_2$ must be reduced to the form: $B.\sin(nt - \phi)$.

Therefore: $B.\sin nt.\cos\phi - B.\cos nt.\sin\phi = a.\sin nt.\cos\delta - a.\cos nt.\sin\delta + b.\sin nt.\cos\epsilon - b.\cos nt.\sin\epsilon = \sin nt.(a.\cos\delta + b.\cos\epsilon) - \cos nt.(a.\sin\delta + b.\sin\epsilon)$.

For all values of t this will be an identity if:

$$B.\cos\phi = a.\cos\delta + b.\cos\epsilon \quad \text{and} \quad B.\sin\phi = a.\sin\delta + b.\sin\epsilon,$$

when $\tan\phi = \frac{a.\sin\delta + b.\sin\epsilon}{a.\cos\delta + b.\cos\epsilon}$, and $B^2 = a^2 + b^2 + 2ab\cos(\delta - \epsilon)$.

Geometrically B can be found from a and b, and the angles δ and ϵ (with the Y-axis), as the diagonal of the parallelogram on a and b, the included angle being $(\delta - \epsilon)$.

In this way an arbitrary number of such vibrations may be combined to a final resultant.

$$\left.\begin{aligned} x_s &= A.\sin(nt - \phi_1) \\ y_s &= B.\sin(nt - \phi_2) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad I$$

in which:
$$\left.\begin{aligned} A^2 &= p^2 + q^2 + 2p.q.\cos(\delta - \epsilon) \\ B^2 &= p^2 + q^2 - 2p.q.\cos(\delta - \epsilon) \end{aligned}\right\} \quad . \quad . \quad . \quad II$$

Furthermore:
$$\left.\begin{aligned} \tan\phi_1 &= \frac{p.\sin\delta + q.\sin\epsilon}{p.\cos\delta + q.\cos\epsilon} \\ \text{and } \tan\phi_2 &= \frac{-(p.\cos\delta - q.\cos\epsilon)}{p.\sin\delta - q.\sin\epsilon} \end{aligned}\right\} \quad . \quad . III$$

From this follows:

$$\tan(\phi_2 - \phi_1) = \tan\Delta = \frac{q^2 - p^2}{2pq\sin(\delta - \epsilon)} \quad . \quad . \quad . IV$$

From *I* we can eliminate t, to find the shape of the orbit described by the emerging vibration. This can be done as follows:

$$\frac{x_s}{A} = \sin nt.\cos\phi_1 - \cos nt.\sin\phi_1$$

and
$$\frac{y_s}{B} = \sin nt.\cos\phi_2 - \cos nt.\sin\phi_2$$

or:

$$\left(\frac{x_s}{A}\cdot\cos\phi_2 - \frac{y_s}{B}\cos\phi_1\right) = \cos nt(\sin\phi_2.\cos\phi_1 - \sin\phi_1.\cos\phi_2)$$
$$= \cos nt.\sin(\phi_2 - \phi_1) = \cos nt.\sin\Delta$$

and

$$\left(\frac{x_s}{A}\cdot\sin\phi_2 - \frac{y_s}{B}\cdot\sin\phi_1\right) = \sin nt(\sin\phi_2.\cos\phi_1 - \sin\phi_1.\cos\phi_2)$$
$$= \sin nt.\sin(\phi_2 - \phi_1) = \sin nt.\sin\Delta$$

Therefore, we have, after squaring and adding both sides of these equations:

$$\frac{x_s^2}{A^2} + \frac{y_s^2}{B^2} - \frac{2x_s.y_s}{AB}\cos\Delta = \sin^2\Delta \quad . \quad . \quad V$$

This equation is that of an ellipse, whose center coincides with the origin *O* of the chosen system of axes; the ellipse is here expressed in the values of two conjugate diameters, one of which coincides with the vertical *OX*-axis, and the other makes an angle Δ with it.

If ψ is the angle of the long principal axis of the elliptical orbit with the OX-axis, then ψ is the rotation $(= 1.\alpha)$ of the solution, and it can easily be proved that this angle $\psi = \frac{1}{2}(\delta - \epsilon)$.

According to *IV*, Δ will be $\frac{1}{2}\pi$ if $\sin(\delta - \epsilon) = 0$, or if $\delta = \epsilon$. From *II* follows, that in this case, in which the principal axes coincide with the co-ordinate axes, these principal axes are equal to $(p + q)$ and $(p - q)$, respectively.

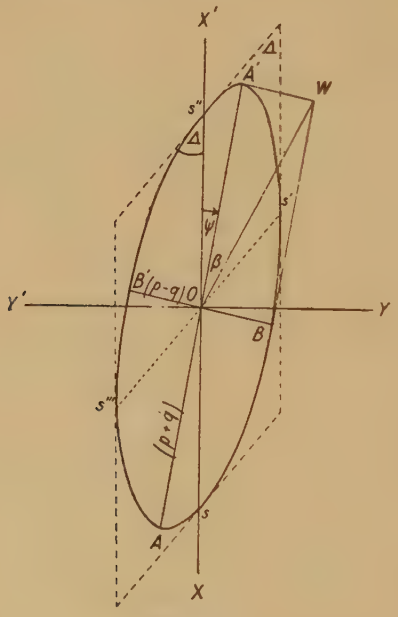


FIG. 76

The minimum value of Δ is reached if $\sin(\delta - \epsilon) = 1$, or $(\delta - \epsilon) = \frac{1}{2}\pi$. The angle Δ has, in this case, the value: $\Delta = \text{arc tan}\,\frac{q^2 - p^2}{2pq}$ and $\psi = \frac{1}{4}\pi = 45°$.

If the angle β (see Figure 76) is measured, then $\tan\beta = \frac{p-q}{p+q}$, and, as will be shown, if β is very small so that $\tan\beta$ may be replaced by β itself—this angle may be represented by:

$$\beta = \frac{\pi(\kappa_L - \kappa_D)\,C.\,l}{\lambda}$$

3a. For this measurement of β a *compensator* is needed, which re-establishes the linearly-polarized light from the elliptically-polarized. A birefringent crystal plate of such thickness d can be used,[1] that for the wave-length λ considered, the phase-difference of the two vibrations being propagated parallel to its principal section is exactly $\frac{1}{2}\pi$, *i.e.* equal to $\frac{1}{4}\lambda$. Indeed, if the axes of the elliptical orbit here are $(p+q)$ and $(p-q)$, respectively, the components are: $x_s = (p+q)\sin nt$

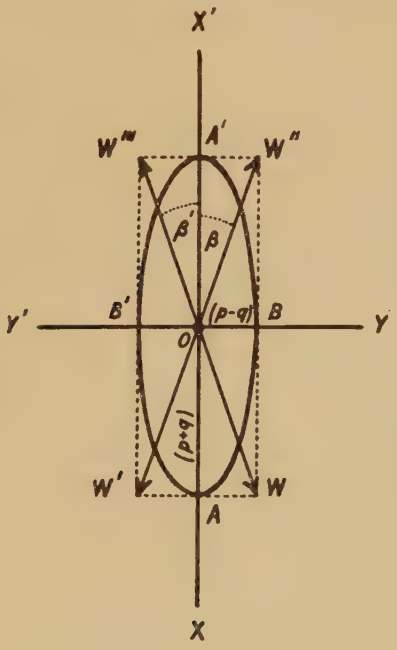


FIG. 77

and $y_s = (p-q)\cos nt$ or: $y_s = (p-q)\sin(nt+\frac{1}{2}\pi)$. Now, if the $\frac{1}{4}\lambda$-plate be so placed that its principal section coincides with the axes of the elliptical orbit of the beam, two cases can be distinguished:

1. *Analogous principal sections are combined (addition).* Then: $x_s = (p+q)\sin nt$ and $y_s = (p-q)\sin(nt+\pi) = -(p-q)\sin nt$.

[1] Chauvin, *J. phys.*, (2) 9, 21, (1890).

These are the components of a *linear* vibration through *O*, the equation of which is $\frac{x}{(p+q)} + \frac{y}{(p-q)} = o$, this linear vibration making an angle β' with the *X*-axis, given by: $$\tan \beta' = \frac{y_s}{x_s} = -\frac{(p-q)}{(p+q)}.$$

2. Non-analogous principal sections are combined (subtraction).

Then: $x_s = (p+q)\sin nt$ and $y_s = (p-q)\sin nt$, which are also the components of a *linear* vibration through *O*, having the equation: $\frac{x}{(p+q)} - \frac{y}{(p-q)} = o$. This vibration makes an angle β with the *X*-axis, given by $\tan \beta = \frac{y_s}{x_s} = \frac{(p-q)}{(p+q)}$. Evidently $\beta = -\beta'$, both angles being those between the diagonals of the circumscribed rectangle WW′W″W‴ of the ellipse (Fig. 77). The measurement of β, therefore, immediately gives us the ratio of the axes of the elliptical orbit.[1]

We can use for the compensation the *Babinet-compensator*. In this instrument the proper shifting of its two quartz wedges gives a combined thickness *d*, such that for each chosen wave-length the path-difference of the vibrations along its principal sections is exactly $\frac{1}{4}\lambda$. However, our Babinet-compensator appeared to be not sensitive enough. In our measurements we have made use of mica plates of $\frac{1}{4}\lambda$ and a so-called Bravais double-plate, as an indicator for the linearly-polarized beam. As it is impossible to have such $\frac{1}{4}\lambda$-plates for each wave-length, we use *four* adjusted, respectively, for mean yellow, red, blue and green colors. The Bravais-plate, which itself is as nearly as possible made of a thickness beyond $\frac{1}{4}\lambda$ also, is cut in two parts, along a direction making 45° with the optical sections, the upper half is then turned upside down and re-cemented with Canada balsam to the lower half along the line of intersection. In this way

[1] If a $\frac{1}{2}\lambda$-plate is combined with the elliptical vibration, then: $x_s = (p+q).\sin nt$ and $y_s = (p-q)\sin\left(nt + \frac{3\pi}{2}\right) = -(p-q)\cos nt$. The result is an elliptical vibration of *opposite* direction of rotation.

the line of intersection ss' (see Figure 78 beneath, to the right) makes in both halves *I* and *II* now 45° with the corresponding principal sections of the plate.

The Bravais double-plate is itself a very sensitive half-shadow-indicator for elliptically polarized light, its two halves becoming identical in intensity only when the incident light is strictly linear polarized. The slightest deviation from this linearity is indicated by a difference in inten-

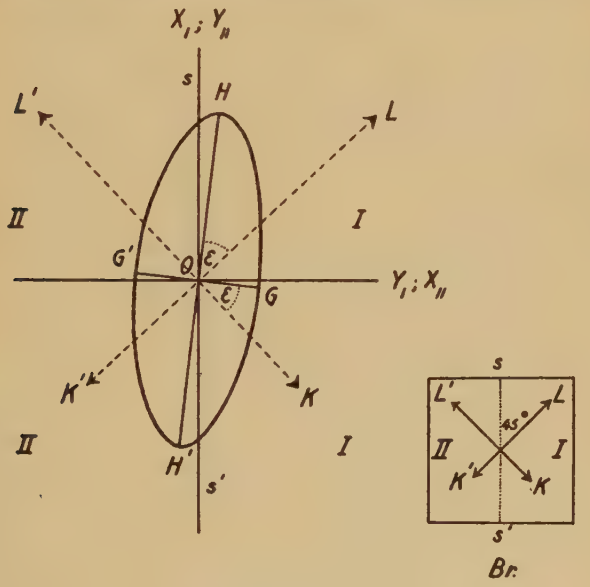


FIG. 78

sity of the halves *I* and *II*; so that in this way it allows a control of the really complete re-establishment of the linear vibration by the proper super position of the $\frac{1}{4}\lambda$-plate upon the elliptical vibration emerging from the polarimeter-tube. On the supplementary measurement necessary to eliminate the errors, caused by the fact that the $\frac{1}{4}\lambda$-plates are *not exactly* correct for intermediate wave-lengths, see the exposition given at the end of this Appendix.

3b. *The Bravais double-plate as an elliptical analyzer.* The analytical treatment of the action of a Bravais-plate on an elliptical vibration will show us some of the

characteristic properties of such a plate, of which properties use is made in its application during the final measurements.

Let the Bravais-plate have a thickness d, and let n_e and n_o be its principal refractive indices; then the vibrations of wave-length λ will, after having passed through it, have attained a phase-difference $\phi = \frac{d}{\lambda}(n_o - n_e)$.

The double plate *Br* is supposed to be permanently fixed to the analyzer, its separation-line ss' making with the principal plane of the analyzer only a small angle α. In Figure 78 the coördinate-axes are OX_I and OY_{II}, and OX_{II} and OY_I, respectively, because in both halves the function of OX and OX'-axes are interchanged. The principal axes of the emerging elliptical vibration may be $a = p + q$ and $b = p - q$; the angle between the axis a of the ellipse and the principal direction OL in the part *I* of the double-plate is called ϵ (see Figure 78).

It is now necessary to find the components of the incident ray and of the emerging one for both halves *I* and *II* of the double-plate, and to determine when their intensities will become identical.

The components of the incident elliptical light on the portion *I* are

in the direction OL: $x_I + x_{II} = a.\cos\epsilon.\sin nt - b.\sin\epsilon.\cos nt$

in the direction OK: $y_I + y_{II} = a.\sin\epsilon.\sin nt + b.\cos\epsilon.\cos nt$

On emerging from the Bravais-plate, both rays have attained a phase-difference ϕ (see above), therefore those components on the first half *I* of the plate will be:

$$\left.\begin{aligned} &x_I' + x_{II}' = a.\cos\epsilon.\sin\frac{2\pi}{T}t - b.\sin\epsilon.\cos\frac{2\pi}{T}t \\ &\text{and} \\ &y_I' + y_{II}' = a.\sin\epsilon.\sin 2\pi\left(\frac{t}{T} - \phi\right) + b.\cos\epsilon.\cos 2\pi\left(\frac{t}{T} - \phi\right) \end{aligned}\right\} I.$$

In the same way, we obtain the components of the rays emerging from the second half of the plate:

$$\left.\begin{aligned} &x_I'' + x_{II}'' = a.\cos\epsilon.\sin 2\pi\left(\frac{t}{T} - \phi\right) - b.\sin\epsilon.\cos 2\pi\left(\frac{t}{T} - \phi\right) \\ &\text{and} \\ &y_I'' + y_{II}'' = a.\sin\epsilon.\sin\frac{2\pi}{T}t + b.\cos\epsilon.\cos\frac{2\pi}{T}t \end{aligned}\right\} II.$$

This becomes evident, as in this second half the directions of the principal sections are interchanged. Now, the principal plane of the analyzer was supposed to make a small angle α with the principal direction of the Bravais-plate. Therefore, the components *I* and *II* will, on emerging from the analyzer, have the values:

$$x_A' = a.\cos\epsilon.\sin\alpha.\sin\frac{2\pi}{T}t - b.\sin\epsilon.\sin\alpha.\cos\frac{2\pi}{T}t$$

$$y_A' = a.\sin\epsilon.\cos\alpha.\sin 2\pi\left(\frac{t}{T}-\phi\right) + b.\cos\epsilon.\cos\alpha.\cos 2\pi\left(\frac{t}{T}-\phi\right)$$

and:

$$x_A'' = a.\cos\epsilon.\sin\alpha.\sin 2\pi\left(\frac{t}{T}-\phi\right) - b.\sin\epsilon.\sin\alpha.\cos 2\pi\left(\frac{t}{T}-\phi\right)$$

$$y_A'' = a.\sin\epsilon.\cos\alpha.\sin\frac{2\pi}{T}t + b.\cos\epsilon.\cos\alpha.\cos\frac{2\pi}{T}t$$

The *intensities* of the above are proportional to the *square* of the amplitudes, therefore:

$$I_I = a^2\{\sin^2(\alpha+\epsilon)-\tfrac{1}{2}\sin 2\alpha.\sin 2\epsilon\}+b^2\{\cos^2(\alpha+\epsilon)+\tfrac{1}{2}\sin 2\alpha.\sin 2\epsilon\} + \tfrac{1}{2}a^2.\sin 2\alpha.\sin 2\epsilon.\cos 2\pi\phi - \tfrac{1}{2}b^2\sin 2\alpha.\sin 2\epsilon.\cos 2\pi\phi + ab\sin 2\alpha.\sin 2\pi\phi.$$

and:

$$I_{II} = a^2\{\sin^2(\alpha+\epsilon)-\tfrac{1}{2}\sin 2\alpha.\sin 2\epsilon\}+b^2\{\cos^2(\alpha+\epsilon)+\tfrac{1}{2}\sin 2\alpha.\sin 2\epsilon\} + \tfrac{1}{2}a^2.\sin 2\alpha.\sin 2\epsilon.\cos 2\pi\phi - \tfrac{1}{2}b^2\sin 2\alpha.\sin 2\epsilon.\cos 2\pi\phi - ab\sin 2\alpha.\sin 2\pi\phi.$$

The *difference* in intensity, $\triangle$, between the two halves is therefore:

$$\triangle = I_I - I_{II} = 2ab\,\sin 2\alpha.\sin\frac{2\pi d}{\lambda}(n_o - n_e) \qquad III.$$

If $\alpha \gtrless 0$, then $\triangle$ can only become *zero* when either a or b is *zero*, *i.e.* if the incident beam is a linearly-polarized one.

As $\triangle$ appears to be independent of ϵ, the difference in intensity of both halves of the plate evidently does not depend on the special position of the Bravais-plate with respect to the principal axes of the elliptical orbit, al-

though on turning the analyzer on which it is fixed, the absolute intensities of both parts will vary with its position. This property is used, as we shall see, in the practical method of measurement.

If $\phi = \frac{1}{2}\pi$ ($\frac{1}{4}\lambda$-plate), the double-plate will be most sensitive; but also for other thicknesses, d, it will serve quite well as a half-shadow-indicator for elliptically-polarized vibrations; but in this last case the angles measured must be corrected, to which we shall draw attention afterwards.

3c. *The Measurement of the Ellipticity.*

As we have already seen, the "ellipticity" of the orbit will be known, when the angle β is determined, because: $\tan\beta = \frac{(q-p)}{(p+q)}$, *i.e.* the ratio of the $\frac{\text{small axis}}{\text{great axis}}$ of the ellipse.

Now if κ_D and κ_L are the fractions of the intensities of the incident *dextro-* and *levo-*gyrate rays, which are absorbed in a solution of a layer of unit thickness, where the concentration is C, we can write

$$\tan\beta = \frac{e^{-\frac{\pi.\kappa_D.C.l}{\lambda}} - e^{-\frac{\pi.\kappa_L.C.l}{\lambda}}}{e^{-\frac{\pi.\kappa_D.C.l}{\lambda}} + e^{-\frac{\pi.\kappa_L.C.l}{\lambda}}} = \frac{1 - e^{-\frac{\pi(\kappa_L-\kappa_D).C.l}{\lambda}}}{1 + e^{-\frac{\pi(\kappa_L-\kappa_D).C.l}{\lambda}}}$$

As long as these angles β are small, $\tan\beta$ may be replaced by β itself, and the ellipticity β can, in that case be expressed by:

$$\beta = \frac{\pi(\kappa_L - \kappa_D).\,C.l}{\lambda}.$$

In this way, by measuring the angle β, the difference of the absorption-coefficients $(\kappa_L - \kappa_D)$ can be determined without any photometrical measurements.

The theory of Drude, which best fits the results of the measurements, teaches, that, as already stated, in the vicinity of an absorption-band the rotation increases to a maximum at the entrance of the band, then rapidly diminishes to zero in the center of the band, and then again gives a maximum at the other end of the band, but with inversed algebraic sign (minimum), after which it increases again towards the zero-axis or even can again become zero and

increase towards the positive side of the rotations. According to Drude's theory, the abnormal rotation $[\alpha]$ can often be represented by an expression of the form:

$$[\alpha] = \frac{A}{\lambda^2 - \lambda_0^2} + \frac{B(\lambda^2 - \lambda_a^2)}{(\lambda^2 - \lambda_a^2) + C.\lambda^2},$$

in which λ_0 is the first absorption band in the ultra-violet, and λ_a that in the visible part of the spectrum under con-

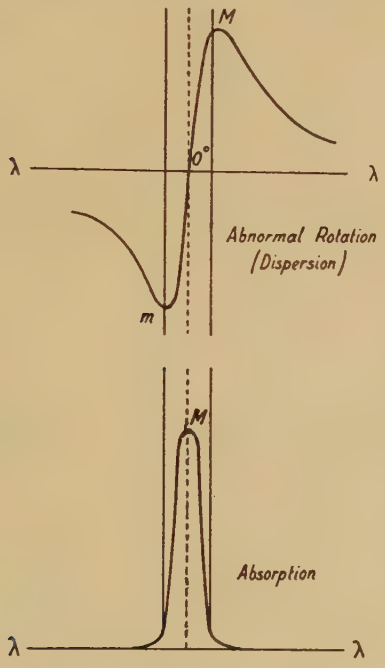


FIG. 79

sideration. Of the three constants: A, B, and C, some can be also negative; thus, for instance, in the case of potassium rhodium trioxalate, A is positive, but B is negative, according to Longchambon.[1] The absorption, however, rapidly increases from the limit of the band to a maximum in the middle of it, and then falls again very rapidly. This absorption determines the "ellipticity" of the orbit, while the anomalous dispersion is given by the first curve.

[1] Longchambon, *Compt. rend.*, 178, 1828(1924).

The maxima of both phenomena never coincide (see Figure 79), so far as experience goes to date (Bruhat).

The measurement of β can be made by using a $\frac{1}{4}\lambda$-plate as compensator, a Bravais double-plate being used as an indicator only, and a Lippich-prism for the measurement of the rotation ψ. Perucca indicated a way for eliminating the inaccuracies introduced by the circumstance that the $\frac{1}{4}\lambda$-plate used is not exact for other wave-lengths than that one for which it has been cut, and also that the rotation ψ cannot be measured directly by a Lippich-prism if the ellipticity is considerable.

3d. *Exact Measurement of the Rotation and Ellipticity, if the latter is considerable.*

The apparatus used is schematically represented in Figure 80. In it P is the polarizer; L the $\frac{1}{4}\lambda$-plate fixed on a divided circle C_1; S is a support, in which the Bravais-plate

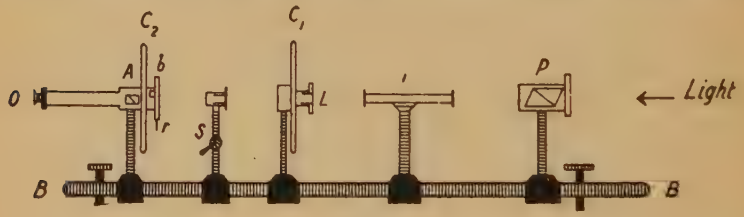


FIG. 80

can be fixed, and which can easily be removed, if necessary; A is the analyzer, consisting of a Lippich's prism; its small half-shadow-prism b is fixed into a ring r, which can be put aside if the Bravais-plate or the $\frac{1}{4}\lambda$-plate must be used. A also is mounted on a divided circle C_2. All parts are fixed on an optical bank B and accurately adjusted. The polarimeter-tube, containing the solution, is indicated by T.

In the apparatus used, the plane of the polarizer is horizontal and remains so during all measurement.

I. The Bravais plate is inserted, after the Lippich-halfshadow has been removed; the plate of almost $\frac{1}{4}\lambda$ is fixed on the compensator-circle, that of the four plates of this kind being chosen whose λ is nearest to that of the luminous source applied. The Bravais-plate is turned in its fitting until the intensity of the two fields, made

equal by turning the compensator-circle, is as weak as possible. The Bravais-plate then has the most favorable position for exact measurements. The reading on the compensator-circle should now be α_0.

II. The Bravais plate is removed, the Lippich-halfshadow, however, inserted; the compensator remains in its former position. The analyzer is turned until both fields of the Lippich-prism have equal intensity. The reading on the analyzer-circle should be then ρ_0. The values α_0 and ρ_0 determine the original adjustment of the apparatus.

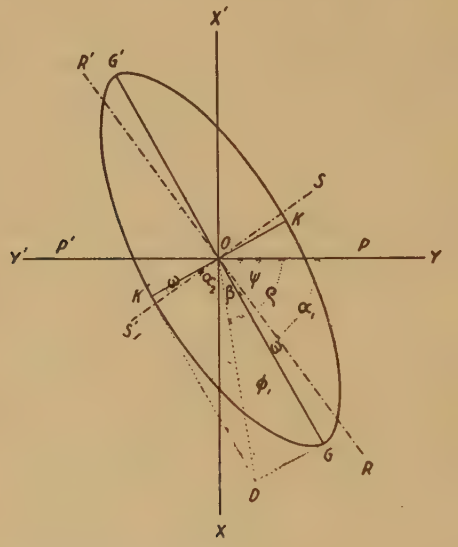
III. Now the tube with the optically-active solution is inserted. The Lippich-halfshadow is removed, the Bravais-plate again inserted. The analyzer is then rotated backwards slightly, so that the intensity of the two halves of the plate is as feeble as possible. The compensator-circle is now turned until both halves have the same intensity.[1] The reading may be then: α_1'. From this value the angle $\alpha_1 = (\alpha_1' - \alpha_0)$ is determined, *i.e.* the angle between the plane of vibration PP' of the polarizer and the direction RR' of greatest velocity in the $\frac{1}{4}\lambda$-plate (Fig. 81). Now the compensator-circle is turned 90° in the positive sense (clockwise). Again it is adjusted in such a way that both fields of the Bravais-plate have equal intensities. The reading on the compensator-circle may then be: α_2'. From this value the angle α_2, *i.e.* the angle between the direction SS' of smallest velocity in the $\frac{1}{4}\lambda$-plate and the plane of vibration of the polarizer PP' is found: $\alpha_2 = (\alpha_2' - \alpha_0)$.

The true rotation ψ, *i.e.* the angle between the greatest axis of the elliptical orbit and the plane of vibration PP' of the polarizer, cannot be measured directly; but it follows from α_1 and α_2. Indeed, if the compensator-plate were *exactly* $\frac{1}{4}\lambda$, RR' would coincide with GG'; but now both directions differ, making a small angle ω with each other (see Fig. 81), if the compensator is placed in such a way, that the linear vibration OD is exactly re-established from the elliptically polarized light. From the figure it is easily seen that $\psi = \alpha_1 + \omega$ and $\psi = \alpha_2 - \omega - 90°$. By addition

[1] In the apparatus used by us, not the divided circle but its vernier is turned. If the rotation is, therefore, *positive* (clockwise), the reading is $< 360°$; for instance, instead of $+2°$, one reads: 358°; etc. The value α_1, therefore, is read on the divided circle between 0° (= 360°) and 270°; and in the same way, α_2 is read between 270° and 180° on the division.

of these equations, ω is eliminated, and it appears, that: $2\psi = \alpha_1 + \alpha_2 - 90°$, or $\psi = \frac{1}{2}(\alpha_1 + \alpha_2 - 90°)$. In this way the true rotation ψ is determined.

IV. The tube with the solution remains in the path of the light-beam; the Bravais-plate is removed, but the Lippich-halfshadow is inserted. The compensator-circle is turned till its reading is again α_1'. The analyzer-circle



PP' = plane of vibration of polarizer
OR = direction of greatest velocity in compensator, because not exactly ¼ λ.
OS = " " smallest " " " " " " ¼ λ.
GG' = greatest axis, *KK'* smallest axis of elliptical orbit.
OD = direction of re-established linear vibration.
Ψ = true rotation; φ = apparent rotation, measured by analyzer, β = angle of ellipticity.

FIG. 81

must now be rotated, if the fields in the Lippich-prism are to have equal intensities, because the linearly polarized beam, having the direction of vibration *OD*, now makes an angle ρ_1 with the plane of vibration of the polarizer *PP'*. If the reading on the analyzer-circle this time be ρ_1', then $\rho_1 = \rho_1' - \rho_0$.

Now the same experiment is repeated, but the compensator-circle is this time turned till its reading is α_2'. By

turning the analyzer till both fields of the Lippich-half-shadow have equal intensities, the reading on its circle may be ρ_2'; then $\rho_2 = \rho_2' - \rho_0$. The true angle ρ is then $= \frac{1}{2}(\rho_1 + \rho_2)$.

From Figure 81 it is easily seen that the angle ϕ_1 is equal to $(\rho_1 - \alpha_1)$; in the same way: $\phi_2 = (\rho_2 - \alpha_2)$, ϕ_2 being thus $-\phi_1$. As the angle $\omega = (\psi - \alpha_1)$, $\omega = \frac{1}{2}(\alpha_1 + \alpha_2) - 45^\circ - \alpha_1 = \frac{1}{2}(\alpha_2 - \alpha_1 - 90^\circ)$. From these two angles ω and ϕ_1, the desired angle β—the tangent of which is the "ellipticity", *i.e.* $\frac{(p-q)}{(p+q)}$ of the elliptical orbit—can be calculated[1] by means of the formula:

$$\cos 2\beta = \frac{\cos 2\phi_1}{\cos 2\omega} = -\frac{\cos 2\phi_2}{\cos 2\omega}.$$

As a control, the relation can be used: $\phi_1 + \phi_2 + 90^\circ = 0$; any deviation from this is a test for experimental errors.

Such experimental errors can occur, for instance, from an insufficient adjustment of the different parts of the equipment used, if reflections at the surfaces of lenses, plates and prisms occur. Because of the small size of the angles to be measured, these adjustments influence strongly the exactitude of the results obtained.[2]

[1] If the compensator were *exactly* $\frac{1}{4}\lambda$, the angle ω would then be 0°, and therefore $\beta = \phi_1$. The general equation for $\cos 2\beta$ is obtained as follows: the components of the vibration emerging from the compensator, may, with respect to its principal directions, be: $x^1 = A \sin(nt - \alpha)$ and $y^1 = B \sin(nt - \beta)$, if α and β are the initial phases for $t = 0$. For the elliptical orbit: $x = a.\sin nt$ and $y = b.\sin(nt + 90^\circ)$, with $\tan\beta = \frac{b}{a} = \frac{(p-q)}{(p+q)}$. According to Billet (*Traité d'Optique physique, II*, p. 61), we have: $\frac{B}{A} = \tan\phi_2$ and $\tan(\alpha-\beta) = -\frac{2ab}{a-b}\cdot\frac{A}{\sin 2\omega} = -\tan 2\beta\,\frac{1}{\sin 2\omega}$; $\sin 2\beta = -\frac{2AB}{A^2+B^2}\cdot\sin(\alpha-\beta) = -\sin 2\phi_1.\sin(\alpha-\beta)$; $\tan 2\omega = \frac{2AB}{A^2-B^2}\cdot\cos(\alpha-\beta) = \tan 2\phi_1.\cos(\alpha-\beta)$. From these relations it follows that: $\frac{\sin 2\beta}{\tan 2\omega} = -\frac{\sin 2\phi_1}{\tan 2\phi_1}\cdot\tan(\alpha-\beta) = -\cos 2\phi_1\cdot\tan(\alpha-\beta)$. But,

as $\tan(\alpha-\beta) = -\tan 2\beta\,\frac{1}{\sin 2\omega}$, it follows: $\frac{\sin 2\beta}{\tan 2\omega} = \frac{\tan 2\beta\cos 2\phi_1}{\sin 2}$,

or finally: $\cos 2\beta = \frac{\cos 2\phi_1}{\cos 2\omega}$ Q.E.D.

[2] For correct adjustment and the inaccuracies involved, *see* Chaumont, *Compt. rend.*, **154**, 271(1912).

If these formulas are to be valid in all cases, it is necessary that the compensator is always turned in a positive sense (clock-wise), starting from the direction of the greatest velocity RR' in the $\frac{1}{4}\lambda$-mica-plate. All angles measured must, of course, be taken with their true algebraic signs.

The angle β thus being known, $\tan \beta = \frac{(p - q)}{(p + q)}$. If $\alpha_1 < \rho$, the elliptical orbit is passed clockwise (positive direction); if $\alpha_1 > \rho$, the motion occurs in the negative sense (counter-clockwise). It is supposed in this case, that the angles α_1 and α_2 differ only slightly from each other, so that the major axis of the elliptical orbit has almost the position OR'.

Only if the angle β is very small, the angle β may be taken for $\tan \beta$ (Bruhat; Cotton). Mostly, however, the method indicated here must be followed for the exact measurement of the rotation—as well as for that of the ellipticity.

As an instance, the following measurements, actually made, may serve to illustrate the said principle.

A very dilute solution of potassium tri-[*d*-tartrato]-chromiate:

$$K_3[Cr^{III}(C_4O_6H_4)_3]$$

in a tube of 5 cm. length, was investigated with sodium light. Subsequently, the following observations were made:

A. *Zero points of the Apparatus.*

1. The Lippich-prism is removed, the Bravais-plate and the mica-compensator are inserted. No tube in the path of the light-beam. The analyzer is placed at 90° with the polarizer; then the analyzer is turned a little until greatest darkness of the field is obtained; subsequently the Bravais-plate is also turned somewhat, so that the different intensity is still detectable and just suited for exact observations. Then the compensator-circle is rotated until both fields of the Bravais-plate have equal intensities. Now the Bravais-plate is again rotated a little and the compensator-circle subsequently, till the fields have again equal intensities and the darkness of the fields is as great as possible. The final position is considered as the initial one of the experiment. The position of the compensator-circle was: 360° 6′ = $(\alpha_0)_1$.
2. Now the Bravais-plate is removed, and the Lippich-prism and the compensator are inserted in the path of the light-beam. The analyzer is rotated until both fields of the Lippich-prism appear of equal intensities. The reading on the circle of the analyzer is: 351° 16′ = $(\rho_0)_1$.

N. B. In rotating the circle clock-wise, the readings decrease here from 360° to 270°, etc.; a turn from 360° to 270° is, therefore, equivalent to a rotation through +90°; etc.

B. *1.* The tube with the solution is inserted. The Lippich-prism is removed, the Bravais-plate and the compensator are inserted. The analyzer is rotated till a maximum darkness is attained, the Bravais-plate rotated slightly, exactly as under A.*1*, then the compensator is turned till equal intensities of both fields are obtained; etc. The final position of the compensator-circle may be: $\alpha_1' = 360° 48'$

2. Now the Bravais-plate is removed and the Lippich-prism inserted. The analyzer is rotated till both fields have equal intensities. The reading on the analyzer-circle is: $351° 10' = \rho_1'$.

Hence: $\alpha_1 = [\alpha_1' - (\alpha_0)_I] = -0° 42'$; the sign is negative, because in our instrument (see above), $(\alpha_0)_I > \alpha_1'$.

$\rho_1 = [\rho_1' - (\rho_0)_I] = +0° 6'$; the sign is positive, because, for the same reason, $(\rho_0)_I$ is $< \rho_1'$.

C. The compensator is turned in a positive or clock-wise direction through 90° (reading about: 270° 6').

1. The solution is removed, likewise the Lippich-prism, the Bravais-plate and the compensator are inserted. The determination of the new zero-points is made, as described in A.*1* and A.*2*.

The final reading of the compensator is: $270° 7' = (\alpha_0)_{II}$.

2. Now the Bravais-plate is removed, the Lippich-prism inserted, etc., as in A.*2*.

Reading on the circle of the analyzer is: $351° 28' = (\rho_0)_{II}$.

D. *1.* The solution is inserted, the Lippich-prism is removed, etc., as under B.*1*.

Reading on compensator-circle is: $270° 41' = \alpha_2''$.

2. After removing the Bravais-plate and inserting the Lippich-prism, etc., as in B.*2*., the reading on the circle of the analyzer is: $352° 21' = \rho_2'$.

Hence: $\alpha_2 = \alpha_2'' - (\alpha_0)_{II} = 360° 6' - 270° 7') - 0° 34' = +90° 1' - 0° 34' = +89° 27'$; and $\rho_2 = -0° 53'$, here again $(\rho_0)_{II}$ being $> \rho_2''$.

We have now obtained the following sets of angles:

$\alpha_1 = -0° 42'$ and $\alpha_2 = +89° 27'$
$\rho_1 = +0° 6'$ $\rho_2 = -0° 53'$

Hence: $\phi_1 = \rho_1 - \alpha_1 = +0° 48'$ $2\omega = \alpha_2 - \alpha_1 - 90° = +0° 6'$
$\phi_2 = \rho_2 - \alpha_2 = -90° 20'$ $2\psi = \alpha_2 + \alpha_1 - 90° = -1° 15'$
$\therefore \psi = -0° 37.5'$.

Remark: Control requires $\phi_1 + \phi_2 + 90^\circ = 0$; as it is here $+0^\circ 28'$, the accuracy is only moderate.

Moreover, we have: $\cos 2\beta$ (2 × ellipticity) $= \dfrac{\cos 2\phi_1}{\cos 2\omega} = \dfrac{\cos 1^\circ 36'}{\cos 0^\circ 6'}$

from which follows: $\beta = 0^\circ 48'$.

Hence: $\tan \beta = \dfrac{(p - q)}{(p + q)} = 0.014$ (= true ellipticity).

The elliptical orbit of the light emerging after having passed through the solution is, therefore, about 70 times as long as it is broad; the rotation is *negative* and $= -0^\circ 37\frac{1}{2}'$.

PART II

METHODS, RESULTS AND PROBLEMS OF PRECISE MEASUREMENTS AT HIGH TEMPERATURES

CHAPTER XIV

Fundamental Principles and Problems

In this second series of lectures I propose to survey methods of precise measurements at very high temperatures, as they have been developed for physico-chemical purposes during the last twenty years in the laboratory of the University of Groningen. Some of these methods have led to results of more general theoretical interest and we shall consider them in some detail; the results that have already been obtained will be discussed in connection with recent theoretical views, and finally I shall point out problems in this field of research that still await experimental solution.

To investigators in pure physics and chemistry, as well as to workers in industrial and technical fields, it is hardly necessary here to dwell upon the value of data of high precision concerning the behavior of matter under these extreme conditions. The lack of sufficiently reliable data of this kind has been felt too long. In fact, the significance of exact data must be evident to everyone interested in the progress of those industries in which high temperatures play a vital part. I will simply mention the whole ceramic and glass-blowing industries, the Portland and other hydraulic cement industries, and the various kinds of metallurgical industries. Such precision work at very high temperatures is also of the greatest interest to pure science. We have a barely sufficient insight into the mutual behavior of chemical molecules, in physical and chemical respects, over an interval of temperature not exceeding a few hundred degrees; yet this rudimentary knowledge is the only source of information from which our present theoretical views concerning the general properties of matter have been deduced. For example, we know very little concerning the valencies of the chemical elements with respect to one another under extreme conditions of pressure or tempera-

ture; also very little as to the relative strengths of inorganic acids at the higher temperatures, and the variations of the physical properties of matter at temperatures of white heat and higher. The literature of these subjects is still full of erroneous and contradictory data.

Our incomplete knowledge, in chemistry and physics at high temperatures, is explained by the particular circumstance that manipulation and experimentation become very complicated as soon as precise data are required. In this connection practical difficulties are encountered in this field that are wholly absent from work at lower temperatures. An experiment that requires only a moderate degree of skill on the part of the observer at usual temperatures, meets serious difficulties even at temperatures of 200° or 300°, and these increase enormously if the temperature is raised still higher; so that at temperatures exceeding 1000° or 1200° the experiment is often impossible of execution unless altogether different methods are developed for its treatment. Even then the measurement will be found to be very tedious, requiring utmost caution on the part of the observer. In general, at these high temperatures the properties of matter become less and less favorable for constructive uses: the best insulators become conductors of heat and of electricity, resistance to mechanical forces diminishes considerably; and above all, reaction-velocities increase to an enormous degree. Thus difficulties are induced and precautions become necessary, of which the investigator working at usual laboratory temperatures has scarcely any conception. The obstacles become still greater when it is necessary to devise methods that shall prove of equal reliability throughout the whole range of say 1700 degrees. Every detail, small and subordinate as it may seem, must be carefully attended to beforehand, if the observer is to avoid the most unexpected and fatal sources of error. The result is that true precision-work at high temperatures requires much time for preparation, and its progress is necessarily slow. Thus it is that many results in the literature prove valueless and often produce an altogether wrong image of the true relations, because many workers

have remained satisfied with methods that give only approximate or even—in several cases—quite erroneous values.

There is a long-felt need for improving the situation. Much excellent and fundamental work in the right direction has been performed during the last twenty years by a number of investigators in America, work that is of the highest value because of its exactness and the rigorous control of all possible sources of error. The work at the Geophysical Laboratory of the Carnegie Institution of Washington, under the critical supervision of its eminent director, Dr. Arthur L. Day, is of particularly notable grade. I myself had the great privilege and opportunity to see and take part in the early development of its methods at the very beginning of my work in this field. In what follows I shall often have occasion to refer to general principles that originated in the experience then gained at the Washington laboratory. In the course of our work during the last fifteen years we have had full opportunity to recognize and to acknowledge the sound basis of that work and the correctness of the criticisms on other methods that are still in use in many places. Without the experience acquired there it would not have been possible for me to develop those methods of research which I shall set forth in the following pages.

The work carried out in my own laboratory relates chiefly to the development of precise methods for measuring, up to 1625°, the temperature coefficient of the molecular surface tension, electrical conductivity, density, and internal friction of liquids; and of high-precision calorimetry of solids up to the same temperature limit. Before discussing these subjects, it is necessary to review briefly the general methods of exact temperature measurement always followed by us, the methods for determining the significant temperatures of phase transitions in matter, as they have been developed in Washington, and to submit those of the results obtained to which we must refer, and compare other results.

Measurements of Temperature up to 1650°

At present the temperatures up to 1650° are always measured by means of thermocouples. These consist, in this

case, of two long wires, one pure platinum and the other an alloy containing 90 per cent of platinum and 10 per cent rhodium, soldered at one end in the oxy-hydrogen flame. This junction *A* is called "the high-temperature junction" or briefly the "hot junction" (see Figure 82). If the two free ends are joined in metallic contact, in a manner to be explained later, and then placed in an ice-box (this is the "cold junction" at *B*, Figure 82) then a thermo-electric current is set up in the circuit thus formed and its intensity will depend upon the difference in potential between the hot and the cold junctions, which potential difference is a very definite function of the difference in temperature between the two junctions. If the cold junction *B* is kept constantly at 0°, then the temperature of the hot junction *A* is measured directly by the potential difference. Of course, other things being equal, this difference in potential is also a function of the particular metals that are used for the thermocouple. A galvanometer *G* placed in the circuit, shows a deflection depending on the intensity of the current passing through (Figure 82). Thermocouples are preferred for this purpose rather than the electrical resistance thermometers, which are very sensitive and useful especially at lower temperatures. In the resistance thermometer one takes advantage of the change in electrical conductivity produced in a thin metallic wire wound upon a spool, if the temperature of the wire is altered. At high temperatures, however, this device compares unfavorably with the thermocouple, due both to its decreasing sensitivity with increasing temperature and particularly to the alterations in form and degree of insulation of the body on

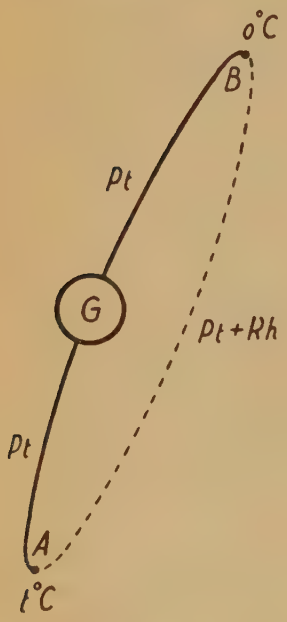


FIG. 82.

which the thin metallic wire is wound. Another drawback to the use of the resistance thermometer at very high temperatures is its greater bulk as compared with the exceedingly small volume of the hot junction of a thermocouple, which can be practically reduced to a single point, and by which also temperature equilibrium between the junction and its environment is almost immediately established. Consequently the resistance thermometer has been totally displaced by the thermocouple in high-temperature work. The indications of the thermocouple are almost instantaneous, especially so if thin wires are used; furthermore its sensitiveness is almost as great at the high temperatures as at the lower ones. Moreover the temperature observations can be easily localized, because the thermocouple can be made in any shape desired and its hot junction quite arbitrarily placed at any point of any experimental device.

However, the thermocouple must be handled very circumspectly. The metals of which the wires are made must be homogeneous in chemical composition as well as in physical properties, throughout their whole extent. Both of them must have high melting points and must not be attacked by either the substances studied, into which the wires are thrust, nor by any reducing atmosphere purposely or accidentally created in the furnace. Having secured homogeneous wires, these may not be bent suddenly at sharp angles, nor may their physical state be altered by drawing them out or hammering them. If properly handled, thermocouples may be preserved unchanged for years, and having been once calibrated, are always ready for use.

Originally Le Chatelier and Barus proposed a thermocouple consisting of a platinum wire and a platinum-iridium alloy wire. This thermocouple is quite inadequate however, for precise measurements, because iridium (and ruthenium) is in air one of the most volatile platinum metals, very probably under intermediary formation of endothermic iridium oxides which at lower temperatures are again decomposed with the deposition of metallic iridium. Sir William Crookes investigated the relative volatility of the different metals of the platinum group, and proved that at 1300° platinum and rhodium are the

least volatile metals, and to an almost equal degree. Palladium is appreciably more volatile at this temperature, while iridium is about 8 and ruthenium about 16 times as volatile as palladium. These facts show beyond doubt, that iridium is not suited for purposes that contemplate keeping the thermocouple wires at a temperature of say 1500° during a somewhat prolonged interval of time. The composition of its platinum-iridium wire will have changed considerably, so that the calibration of the thermocouple is completely lost. Moreover, the iridium will be redeposited on the cooler parts of the furnace and the wires of the thermocouple, and this "infection" invalidates the calibration. On the other hand, the small difference in volatility between platinum and rhodium make these metals particularly well suited for combining in the second wire of the thermocouple. If well treated, these platinum-rhodium thermoelements can be used for a long time before recalibration becomes necessary. It now becomes necessary carefully to avoid in the furnace any further presence of iridium; so that the heating coil of the furnace and all the other platinum parts used in it, such as crucibles, cylinders, diaphragms and tubes, must be prepared from a specially purified platinum. For this purpose Heraeus in Hanau furnishes us with his so-called "Tiegel-Platin" which, according to analysis by Mylius' method, applied to larger masses of the metal under examination, is guaranteed to contain less than 0.1 per cent iridium. Even with these precautions, it appears necessary repeatedly to recalibrate the thermocouples used in the investigation, particularly after prolonged use at higher temperatures. If this precaution be neglected, very serious errors in the temperature indications may be introduced into the results, as experience has often demonstrated.

For information as to the manner in which the homogeneity or possible infection of the thermocouples is to be tested, I would refer to my *Anleitung*.[1]

[1] I shall have repeated occasion to refer to a little work on precise physico-chemical measurements at high temperatures, which I published in German some sixteen years ago, under the title *Eine Anleitung zur Ausführung exakter physico-chemischer Messungen bei höheren Temperaturen*, 152 p., 35 fig. (Groningen, 1913). This work will be referred to simply as *Anleitung*. Since much progress has been made since that date, it seems desirable to rewrite this little book, although it contains many details that are still of value for work of this kind.

The calibration of these thermocouples is of fundamental importance. It is best done by determining a series of fixed points such as known melting and transition points for certain salts, metals and other compounds which have been already determined precisely on the adopted standard temperature scale. In our work the adopted scale is that of the nitrogen gas thermometer at Washington, based on Day and Sosman's fundamental work thereon.[1] Since metals at higher temperatures may infect the thermocouples through volatilization, and since many of them can be used only in a reducing atmosphere—which must always be avoided with platinum thermocouples—the writer has in recent years, used only salts and artificial silicates for this calibration, since the hot junction of the thermocouple may be inserted in those compounds without protection. The substances we have usually employed in calibrating are:

Sodium molybdate (Na_2MoO_4):
1st transformation point, EMF = 3675 μv,[2] t = 444°.
2nd transformation point, EMF = 5108 μv, t = 588°.
3rd transformation point, EMF = 5611 μv, t = 637°.
Melting point, EMF = 6132 μv, t = 687°.

Sodium tungstate (Na_2WO_4):
Melting point, EMF = 6287 μv, t = 702°.

Sodium chloride (NaCl):
Melting point, EMF = 7333 μv, t = 800°.

Barium chloride ($BaCl_2$):
Melting point, EMF = 9111 μv, t = 960°.

Lithium metasilicate (Li_2SiO_3):
Melting point, EMF = 11944 μv, t = 1201°

Artificial Diopside ($CaMg_2(SiO_3)_2$):
Melting point, EMF = 14231 μv, t = 1391°

Artificial Anorthite ($CaAl_2(SiO_4)_2$):
Melting point, EMF = 16162 μv, t = 1551°

Barium metasilicate ($BaSiO_3$):
Melting point, EMF = 62801 μv, t = 1604°

[1] A. L. Day and R. B. Sosman, *Carnegie Inst. Wash. Publ.*, No. 157 (1912); *Am. J. Sci.*, 33, 517 (1912).

[2] The EMF of the thermocouple is always expressed in microvolts, μv, = 10^{-6} volts.

If these fixed points are determined with all necessary precaution,[1] they are quite sufficient to characterize the special behavior of the thermocouple employed. For lower temperatures one can use the melting points of naphthalene (217.7° = 1584 μv) and of benzophenone (305.4° = 2365 μv). This method permits us to determine the deviations in the indications of these thermocouples from the standard used by Day and Sosman, and their homogeneity may be tested at any moment; the EMF given is that of the standard element. Day and Sosman also determined the precise melting points of a number of pure metals, the following may be given here:

Zinc,	418.2°	Nickel,	1452.3°
Antimony,	629.2	Cobalt,	1489.8
Silver,	960.0	Palladium,	1549.2
Gold,	1062.4		

The melting point of platinum on this scale, is 1755°.

The electromotive force of the thermocouples is measured by a compensation method, employing a potentiometer and a calibrated galvanometer of very high sensitivity. The needle galvanometers with temperature scale that are ordinarily used and are generally on the market, are quite unsuited for this work at least for accurate scientific temperature measurements. The principle of potentiometer measurements is too well known to need explanation in this place.

In our work we always use Dieselhorst potentiometers having only three decades, as built by O. Wolff of Berlin. They are free from all parasitic thermoelectric effects and are of excellent construction. We also use an additional ten-step resistance made by the same firm, which permits the use of currents of exactly 0.1, 0.01, 0.001 and 0.0001 amperes from a Weston-Normal-element used as a standard cell. A commutator that is also free from all thermoelectric effects enables us to make readings with a direct and a reversed current. That portion of the EMF not compensated by the three-decade resistance is measured by the deflections of the calibrated galvanometer. This instru-

[1] For the methods to be used, see F. M. Jaeger, *Anleitung*, p. 13–22.

ment is a highly sensitive vibration-free moving-coil galvanometer of short period and of high internal resistance Of late years we have employed the excellent instruments designed by W. Moll or by F. Zernike and put on the market by P. J. Kipp & Sons of Delft. Further details of the arrangement of the instruments and the special ice-box used for the zero point of the thermocouples, will be found in my *Anleitung*.[1] Formerly the deflections of the galvanometer were read by means of a telescope but today they are always read off from a transparent Hartmann and Braun celluloid scale on which the image of the galvanometer mirror is projected by a beam of light that first passes through a 45° prism and a lens. The external resistance and the distance between the galvanometer and the scale are brought into such adjustment that a scale-deflection of 1 mm. corresponds to 1 microvolt. A potentiometer of five decades is needed only for such extremely precise work as that of our calorimetric determinations.

Experience has shown that, when thermocouples are used to measure temperatures above 1200° in resistance furnaces having the heating coil placed inside the furnace and using direct current, it is absolutely necessary to protect the thermocouples against the ions liberated in the air of the furnace by the intense heat, and against the free electrons expelled from the glowing metallic wires. These circumstances make the air within the furnace electrically conductive. Under the potential difference then present electrically-charged particles are moved toward the measuring instruments (thermocouples), and the electrical conductance causes an irregular swinging of the galvanometer needle which makes it impossible to obtain precise readings. Therefore it is necessary to shield the thermocouples by surrounding both them and the crucible with a Faraday-cage of platinum. This cage is a tube in contact with the crucible and connected with a grounded platinum-wire spiral about the porcelain tube protecting the thermocouple. As was pointed out by White, it is also necessary to place all the measuring instruments on metal plates

[1] F. M. Jaeger, *op. cit.*, p. 13–22.

mutually connected by metallic wires and grounded, in order to eliminate all disturbances due to erratic currents. Of course, all the junctions in the measuring device must be perfectly insulated and suspended by means of silk cords or supported by glass rods carrying mica rings.

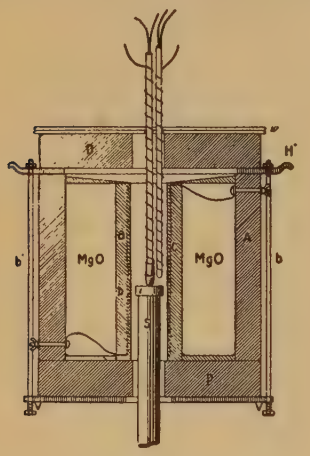


FIG. 83

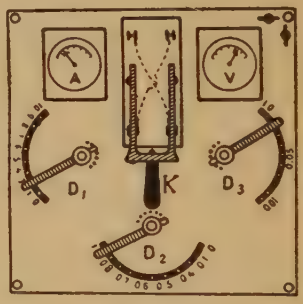


FIG. 84

The furnaces employed consist of a core of burned magnesite (Figure 83, *a*, *b*, *c*) with an iridium-free platinum coil of 1.2 mm. wire (about 200 gm. weight) that is wound spirally by a method described in the *Anleitung*, loc. cit. The advantage of placing the coil inside the furnace consists in the fact that the temperature of the inner portion can be raised to 1625° without danger of melting the wire. Changes in the intensity of the heating current also will be followed by the desired temperature changes more rapidly than when the coil is placed on the outside of the magnesite cylinder. The whole furnace is inclosed by a cylinder of fire brick (Figure 83, *A*), and the space between the brick and the core is filled with finely powdered magnesia. If, as in calorimetric work, the furnace must be perfectly insulated against loss of heat then the whole furnace must be enclosed in double-walled mantles of zinc or copper carrying a rapidly circulating current of cold water. The direct current (about 110 volts) is controlled through a large decade resistance box (see Fig. 84).

Heating commonly starts at about 40 amperes; but the necessary current soon drops to about 20 amperes at higher temperatures. With some practice and skill, it is possible to regulate the temperature of these furnaces so accurately as to keep it within limits of one degree for long intervals of time. It is a very important fact that only a very small portion of the furnace interior is without a temperature-gradient, so that only within that small space does the furnace behave as a true thermostat when the heating current is held constant. Only within this limited space does the furnace have a strictly uniform temperature. The air column of the furnace is hottest in the immediate vicinity of the cylindrical wall containing the heating coil; the upper and lower ends of the column are cooler. This temperature distribution can be improved by using suitably located diaphragms; or by winding the heating coil in somewhat closer spirals at either end than in the middle of the furnace; or by using removable supplementary heating coils at either end. In the middle of the hot air column there is a short cylindrical space 4 to 6 cm. long within which the temperature is practically uniform. All measurements should be made in this constant-temperature space (see Figure 85, shaded area), and here should be placed the crucibles, charges, and the like. An investigator who employs sufficient care can keep the temperature of this little space constant within one degree, even at working temperatures of 1625°. The large crucibles of former days are now replaced by very small ones, 1 cu. cm., in order properly to use this very limited space in the furnace. The refinements of modern temperature measurement en-

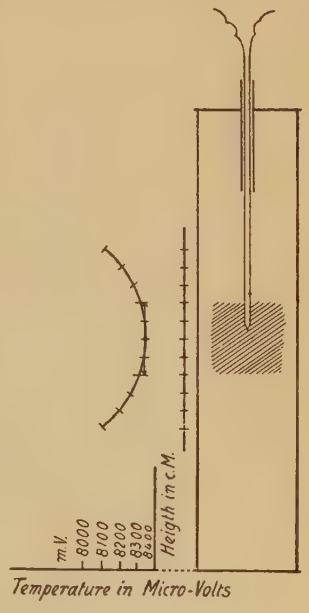


FIG. 85

able us to secure determinations with these small crucibles that are much more accurate than those formerly obtained with the large ones.

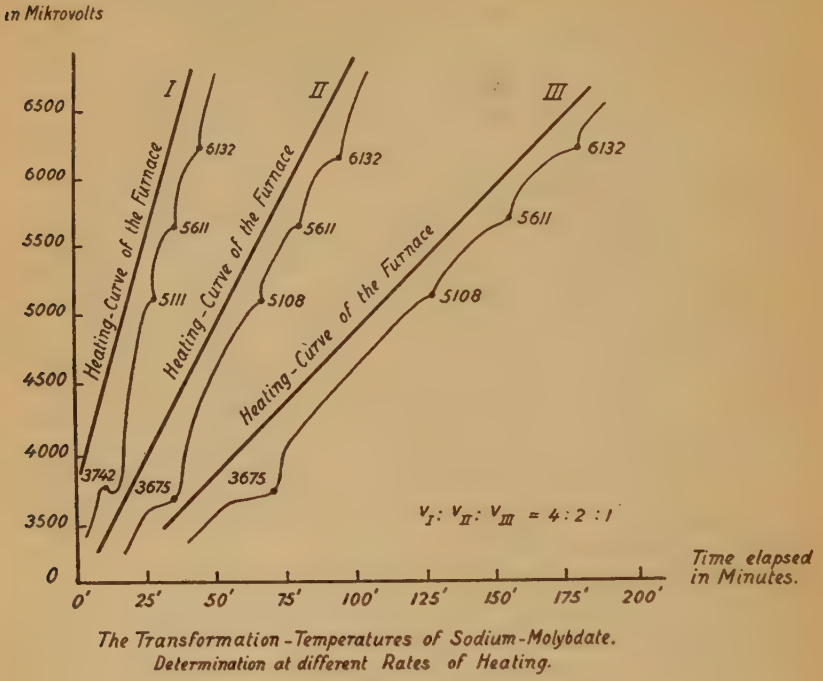


FIG. 86

The hot junctions of the thermocouples must be adjusted in this restricted uniform-temperature space; and on gradually varying the temperature of the furnace, it is here only that really exact and reproducible measurements of melting points and transition points can be determined by means of the heating curves.

The extent of this space must be determined before starting the experiment because its position within the furnace changes somewhat, particularly after experiments of long duration or after a prolonged use of the furnace. If the crucible is placed within this space, the data for melting or transition points appear to be really independent of the rate of heating and completely reproducible. Figure 86 presents some characteristic curves obtained with

sodium molybdate (Na_2MoO_4) at different heating rates. It also serves to illustrate the degree of independence of melting points with respect to heating-rate. In such experiments at least two thermocouples must be used: one placed in the furnace chamber and the other inserted in the charge. They are read alternately by means of a specially constructed commutator that is free from all accessory thermoelectric effects. Figure 86 presents both furnace curves and charge curves and it is clear that the discontinuities in the latter all lie at practically the same temperatures, although the rates of heating for the three curves are in the ratio 4:2:1. If all mentioned precautions are properly taken, the measurements are perfectly reliable and reproducible.

When temperature measurements above 1650° are to be made, thermocouples made of metals having higher melting points than the platinum-rhodium thermocouples must be used; or one must employ radiation pyrometers, instruments based upon the general relations between radiation and temperature as deduced from the laws established by the work of Kirchhoff, Boltzman, Wien, Planck, Stefan, and others. Other metals that are suitable for thermocouples, *e.g.* molybdenum, tantalum, are of restricted number because most of them are readily attacked at high temperatures by nearly all substances, such as oxygen, carbon, nitrogen; nor can they be soldered firmly together, and they must be used in a vacuum. Therefore, under the conditions here considered, both science and industry have recourse to the optical or radiation pyrometers. These instruments now are usually of the type devised by Féry, Wanner, and Holborn and Kurlbaum. The latter instrument combines the sensitivity of Wanner's instrument with certain specific advantages for high-temperature work, since a slight modification of it permits one to look into the furnace and to control—within limits—what is taking place within the charge as shown by direct observation. By means of this instrument the radiation of the incandescent body under consideration is compared with the radiation of the wire of a calibrated incandescent lamp whose temperature is kept at a fixed

degree by controlling its heating current. By inserting a 45° glass prism before the objective of the telescope (Figure 87, *P-L*) it is possible to adjust the instrument so as to permit simultaneous visual observation of the interior of the furnace also. One must keep in mind, however,

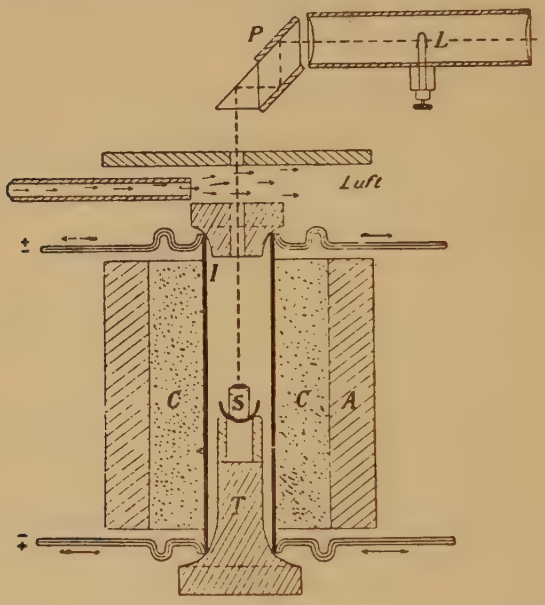


FIG. 87

that the determination of temperatures by means of such radiation-pyrometers is far from being as accurate a method as that employing a thermocouple.[1] The percentage accuracy of this method of measuring the radiation is considerably less than that of the thermo-electric method. The variations in the physiological sensitiveness of the human eye and the deviation of the properties of the radiating body from those of a true "black body" combine to make the indications of the optical pyrometer much less exact than those of thermocouples. One cannot avoid errors and uncertainties amounting to 20 degrees in either direction, when

[1] Concerning the curious influence of the anisotropy of emmission of a glowing crystal on its apparent radiation-temperature, when a polarizer is combined with the Holborn-Kurlbaum pyrometer, *see* F. M. Jaeger and A. Simek, *Proc. Acad. Sci. Amsterdam*, 16, 799 (1914). A tourmaline crystal at 900° had an apparent temperature about 15° higher, in the direction of maximum adsorption, than in a direction perpendicular thereto, which is in full agreement with Kirchhoff's emission law.

using the optical pyrometer; with our measuring device differences of 0.1 of a degree can be detected with accuracy even in the region of 1600°. The radiation method seems to be sufficiently reliable only for the determination of melting points and of certain eutectic points of binary systems. As to the vacuum-furnaces used for temperature work at 2000–3000° I must refer to my *Anleitung*.[1] In general, real precise measurements, properly so called, are only possible within a temperature interval ranging from the lowest obtainable temperatures up to about 1650°. We shall confine our attention to the measurements at or near this upper limit.

In conclusion I would add a few remarks concerning the application of these methods to some problems in chemistry. During the past twenty years their most important use—and again principally at the Geophysical Laboratory of the Carnegie Institution—has been for studying heterogeneous equilibria in systems of one, two and three components. The very great difficulties encountered at the phase-transition-points of borates, silicates, and the like, due to the unfavorable combination of small latent heat, small thermo-conductivity, low rate of crystallization and high viscosity, led to the development and refinement of the measuring methods just described. It would be interesting, at this date, to reinvestigate a number of the phenomena of binary and ternary metallic systems, applying the modern improved methods. This might develop many new and surprising facts and phase-transitions which so far have escaped observation by the cruder methods heretofore employed. Such work might prove to be of the greatest importance for the metallurgical industries also.

Chemical investigations of the silicates were initiated primarily for the purpose of explaining, if possible, the processes of magmatic solidification; but the investigations of systems containing the oxides of calcium, magnesium, aluminum, potassium, and sodium in addition to SiO_2, have already revealed many facts that have helped to explain numerous phenomena previously observed in ceramics, glass-making and cements.

[1] F. M. Jaeger, *Anleitung*, p. 48–52.

Work of this kind is carried on according to one of two principal methods. The more rapid one and the preferable one, if it is suitable, consists in determining the discontinuous changes in the thermal capacity of the material system with continuously varying temperature, and uses the so-called heating-curves. Where there is a strong tendency for retardation phenomena to occur, viz., undercooling, supersaturation, superfusion, and the like, such as characterize the borates and the silicates, cooling-curves are not feasible. The details of the method of heating-curves are given in my *Anleitung*.[1]

The second method consists in keeping the material system, whose chemical composition is assumed to be precisely known, at a definite constant temperature for a period sufficiently long to determine the establishment of its thermo-equilibrium. The system is then "quenched" by immersing it suddenly in cold mercury or a non-volatile oil. This sudden drop in temperature diminishes the reaction-velocity so markedly that the state of equilibrium reached at the higher temperature is practically conserved, because there has been no time for it to lose that condition. The resulting product is carefully examined under the microscope, and the possible presence or absence of a glassy substance is carefully checked up. If glass is present it signifies that the system was partly or even completely molten at the higher temperature. If the mass is holocrystalline it means that no liquid phase had as yet appeared at that temperature. Of course this holds only for such systems as the borates or silicates, whose speed of crystallization is low. The experiment is now repeated at a series of somewhat higher or lower temperatures; and it is thus attempted to approach, from either side, the temperature at which the whole sample consists either of glass or of crystallized material. This enables one to determine the temperature at which a liquid phase begins to appear or ceases to exist. In this manner the equilibrium temperature can be gradually narrowed down within two extremes that lie close together and thus can finally be determined to any desired degree of accuracy.

[1] *Ibid.*, p. 55–74.

The quenching furnace used in these experiments is shown in cross section in Figure 88. The sample, wrapped in platinum foil, is suspended by a thin wire in the region of uniform temperature, and at the desired moment is released by causing a strong electric current to melt the suspension wire. This was the method employed by Shepherd and Rankin for determining the fields of existence of

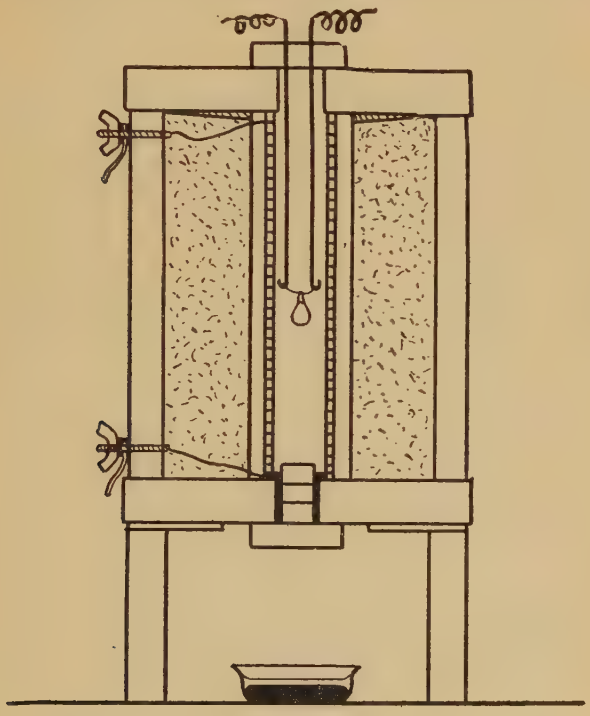


FIG. 88

a large number of compounds in the ternary system of SiO_2, CaO, Al_2O_3. It has rendered much service also in establishing the solid-liquid curve for the isomorphous series of the feldspars between anorthite and albite. It has also been used for studying one-component systems in which polymorphism plays a part, *e.g.* with SiO_2 itself; the method has also been successfully used for disentangling highly complicated equilibrium relations between the different modifications.

CHAPTER XV

The Temperature Coefficient of the Surface Tension of Liquids Between −80° and +1625°

We shall now proceed to consider the particular subject of this series, *i.e.* the application of the foregoing principles in complicated measurements.

We shall begin with the method developed for the precise measurement of the temperature coefficient of the surface tension of liquids at temperatures up to 1625°. A precise knowledge of the free surface energy of liquids and its dependence on temperature is, as is well known, one of the most urgent needs of modern physical chemistry, because it supplies us with data that are intimately connected with the whole internal structure of liquids. The application of the laws of thermodynamics in this field of research,[1] especially has brought to the fore the particular significance of temperature variation for the mode of action of the capillary forces. It is desirable to recall here these theoretical views which lie at the very basis of all our work.

Let χ be the work (in ergs) to be done against the capillary forces if the surface S of a liquid is increased by 1 sq. cm., and let W_s be the amount of heat required to produce this increase assuming it to be performed isothermically. Then, if c is the specific heat of the liquid at the absolute temperature T considered, and S is its surface, thermodynamics teach us that

$$W_s = -T/J \cdot \frac{\partial \chi}{\partial T} \qquad \text{and} \qquad \frac{\partial c}{\partial S} = -T/J \cdot \frac{\partial^2 \chi}{\partial T^2}$$

In these equations J is the mechanical equivalent of the zero-point calorie,[2] that is 41.977×10^6 ergs. Experience

[1] W. Thomson, *Proc. Roy. Soc. London*, **9**, 255 (1858); *Phil. Mag.*, (4) **17**, 61 (1859); W. Gibbs, *Thermodynamische Studien*, p. 66 (Leipzig, 1892); A. Einstein, *Ann. Physik*, **4**, 513 (1901); J. D. van der Waals, *Z. physik. Chem.*, **13**, 713 (1894).

[2] Since the zero-point calorie is 1.005 times the mean calorie, the value of J for the latter ought to be 41.77×10^6 ergs.

has shown that $\partial\chi/\partial T$ is always negative, the surface tension being found to decrease with increasing temperature. W_s therefore is always positive, which means that an isothermal increase of the surface of the liquid requires the addition of heat. An adiabatic increase of the liquid surface would then cause its temperature to fall; in fact $-\partial\chi/\partial T$ is the change of entropy of the liquid, if its surface is increased from S to (S + 1) sq. cm., and the total surface energy, U_s, per square centimeter of the liquid therefore equals

$$U_s = \left(\chi - T\frac{\partial\chi}{\partial T}\right)$$

From the second equation it is at once evident that the specific heat c of the liquid is independent of its surface S, if $\partial^2\chi/\partial T^2 = 0$. But this is only true when $\partial\chi/\partial T$ is constant, that is, when χ is a linear function of the temperature. It is, therefore, very important to determine whether χ is directly proportional to the temperature T or not. If this is not the case, it should follow that c is a function of the extent of the surface S, the liquid in the surface layer having a heat capacity different from that of the bulk of the liquid. In contrast with the classic theories of capillarity by Laplace and Gauss, this fact would imply that the surface energy of a liquid is not merely potential but, in part at least, kinetic in nature. Since this latter view is apparently the more probable and more nearly correct one, it may be supposed that precise measurements will not show, in general, any linear relationship between χ and T.

Although these few remarks make evident the importance of an exact determination of $\partial\chi/\partial T$, the problem has aroused still greater interest in recent years, among chemists also, because of the relationship that seems to exist between the temperature coefficient and the internal structure of such liquids. It seems as though it will enable us to draw some conclusions concerning their true molecular weights.

Eötvös[1] established experimentally a law that bears his name, which gives—with the necessary precautions—a

[1] R. von Eötvös, *Ann. Physik*, 27, 448 (1886); Stefan, *ibidem*, 29, 555 (1886); J. D. van der Waals, *Z. physik. Chem.*, 13, 713 (1894); A. Brandt, *Drude's Ann. Physik*, 10, 783 (1903).

numerical relationship between the true molecular weight of the liquid and the temperature coefficient of its so-called molecular free surface energy μ. If χ be the surface tension of a liquid expressed in dynes per cm. or in ergs per sq. cm., measured at the temperature T, and if d be its density and M its molecular weight, then Eötvös was able to show that the following relation holds very closely for all liquids:

$$\chi\left(\frac{M}{d}\right)^{2/3} = k\,(T_0 - T)$$

In this expression M/d is the molecular volume v of the liquid, *i.e.* the volume occupied by 1 gram-molecule; if this is a sphere the molecular surface of the liquid is proportional to $v^{2/3}$. If the product $\mu = \chi v^{2/3}$ is called the free molecular surface energy of the liquid, and T_0 is a temperature close to the critical temperature of the liquid, then it would seem that k is a universal constant for all "normal" that is, non-associated liquids, being independent of the special nature of the liquid and having a mean value of about 2.2, as was stated by Ramsay[1] and Guye[2] and their collaborators, and also by ourselves.[3] According to this relationship, the work required to produce the surface of a sphere containing 1 gram-molecule of any liquid similarly depends on the temperature. The same relationship exists in the case of the work required, according to Avogadro's law, to produce 1 gram-molecule of any given gas under constant temperature, the work required being in this case directly proportional to the absolute temperature. In applying Eötvös' formula the factor $(T_0 - T)$ must not be too small; *i.e.* the formula holds only for temperatures at a sufficient distance from the critical temperature, θ_0.

As regards the theoretical basis of the relation here considered it may be remarked that, according to the potential

[1] W. Ramsay and J. Shields, *Z. physik. Chem.*, **12**, 433 (1893); W. Ramsay and W. Aston, *ibidem*, **15**, 98 (1894); Grunmach, *Drude's Ann. Physik*, **15**, 401 (1904).

[2] P. A. Guye and others, *J. chim. phys.*, **3**, 38 (1905); **5**, 81, 97 (1907); **9**, 505 (1911); and elsewhere. P. Walden, *Z. physik. Chem.*, **75**, 555 (1911); P. Walden and Swinnes *ibidem*, **79**, 700 (1912); J. L. Morgan and collab., *J. Am. Chem. Soc.*, **30**, 360, 1055 (1908); **33**, 349, 643, 657, 672, 1060, 1275, 1713 (1911); **35**, 1249, 1505, 1750, 1759, 1821, 1834, 1845, 1856 (1913); **37**, 1461 (1915); **39**, 2151, 2261, 2275 (1917); *Z. physik. Chem.*, **63**, 151 (1907); **64**, 170 (1908); and elsewhere.

[3] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1–214 (1917).

theory,[1] the work required to bring a molecule of liquid from the interior to the liquid surface layer—supposing that neither the internal nor the rotational energy of the liquid is altered—is equal to the work required to bring it from the surface of the liquid into its co-existant vapor-phase. The first term represents the molecular free surface energy, the last term is the energy equivalent of the latent molecular heat of vaporization of the liquid; therefore both must be proportional to each other, the coëfficient of the proportionality depending on the special system of fundamental units adopted. Now, if the "theory of corresponding states" of Van der Waals[2] is considered to hold for the cases here considered, *i.e.* if the boiling points T_b of all liquids ($= \frac{2}{3}$ of the critical temperature θ_0) can be considered to be real "corresponding" temperatures,[3] then according to Trouton's rule,[4] the ratio Q/T_b of the latent molecular heat of vaporization Q and the absolute boiling point T_b not only will be identical (about 20–22) for all liquids, but the same equality will exist for all other equal "reduced temperatures" $\theta = T/\theta_0$. The same must therefore be true also for the ratio μ/T, so that one may write $\mu/T = k(\frac{T_0}{T} - 1)$; and k must now be independent also of the special nature of the liquid, if T be sufficiently distant from T_0 and therefore from the critical temperature θ_0.

If k now varies appreciably for different liquids this signifies, first of all, that there is a strong discrepancy in

[1] Stefan, *loc. cit;* A. Brandt, *loc. cit.*

[2] The law of corresponding states of van der Waals is expressed by the equation:

$$(\pi + 3/\phi^2)(3\phi - 1) = 8\theta$$

where π, ϕ and θ are "corresponding" pressures, volumes and temperatures, *i.e.* pressures, volumes and temperatures p, v, and T expressed as ratios of the critical ones. Thus: $\pi = p/\pi_0$; $\phi = v/\phi_0$; and $\theta = T/\theta_0$, in which π_0, ϕ_0, and θ_0 are the critical pressure, volume and temperature, respectively, of the liquid (gaseous) matter.

[3] Guldberg, *Z. physik. Chem.*, 5, 374 (1890); see also Young, *Phil. Mag.*, (5) 34, 507 (1892).

[4] Trouton's rule is $Q/T_b \cong 20$ or 22. It holds only for ordinary temperatures. As Nernst has shown (*Gött. Nachr.* 1906; also Bingham, *J. Am. Chem. Soc.*, 28, 723 (1906)) this ratio increases slowly with the temperature. If the law of corresponding states holds, Trouton's rule can be expressed in the form: $Q/T = R \cdot \frac{\partial \ln \pi}{\partial \ln \theta}$, from which it follows that Q is proportional to T at all corresponding temperatures, the proportionality factor being independent of the special nature of the liquid.

the law of corresponding states, which discrepancy may be due, perhaps indirectly, to a polymerization of the liquid, *i.e.* a change of its molecular weight. In many cases, therefore, it is dangerous to calculate the degree of association by means of k's variations from its "normal" value. Up to the present, however, experience indicates that k's variations are influenced but slightly by an actual deviation from the law of corresponding states, and much more strongly by some possible polymerization of the liquid (alcohol, carboxylic acids, and the like). This, then, must be the reason for the experience that in a large number of cases the values of the molecular weights of liquids, as deduced from the deviations of k from its normal value of 2.2, appear actually to correspond to their true values as determined by other methods, in spite of the failure of the law of corresponding states. As is the case with Trouton's rule, one must use special caution—according to Nernst—in all cases where liquids are considered at extreme temperatures or have either very low or very high boiling points. Walden[1] and myself[2] verified this latter fact experimentally for the case of the neutral esters of glycerol and the higher fatty acids.

The results obtained with molten inorganic salts are of special interest because of the relatively simple constitution of the liquids. The investigation to be described was begun with the intention of explaining the relations between chemical composition and the internal structure of these liquids. Here the case is more complicated, to the extent that one is probably not justified in supposing that the law of corresponding states can be valid under these conditions; so that it is not yet possible to conclude, from anomalous values of $\partial\mu/\partial T$, that a state of de- or polymerization is present when we are dealing with systems in an advanced state of electrolytic dissociation and probably having a more or less regular orientation of the electrically-charged ions in the surface layer.

In any case, the first task to be undertaken was to develop an accurate method for measuring surface tensions

[1] P. Walden, *Z. physik. Chem.*, **75**, 555 (1911).
[2] F. M. Jaeger, *Z. anorg. Chem.*, **101**, 70ff (1917).

over a wide range of temperatures. The method must give exact and reproducible results whose precision would be as great at the highest temperatures investigated (1625°) as it is for lower temperatures.

A large number of methods have been proposed for measuring the surface energy of liquids; but most of them are not suited for precise work at high temperatures, as will be clear from the difficulties set forth in the preceding chapter.

Under the circumstances predicated it was not possible to use the flowing liquid method developed by Rayleigh,[1] nor the vibrating beads of Lenard,[2] nor the capillary waves method of Thomson.[3] The measurement of the radii of curvature of liquid drops, the adhesion plates method, and even Tate's method by weighing falling drops,[4] all appeared unsuitable in this case. Up to 700° the method of capillary rise in tubes has been used;[5] the writer also made a number of such determinations, but finally abandoned the whole method because it was impossible to maintain a constant temperature throughout the extent of the tube and because, at higher temperatures, the capillary tubes all suffered corrosion by the molten salts, so that their calibration was lost and the molten salts polluted by materials detached from the tube walls.

Because the uniform-temperature region within the furnace is very restricted, the successful method must develop symmetrically-shaped apparatus of very small dimensions. This consideration finally decided us to employ a method suggested by Simon, Cantor, and others,[6] based upon the

[1] Rayleigh, *Proc. Roy. Soc. London*, **29**, 71 (1879); **34**, 130 (1882).

[2] Lenard, *Ann. Physik*, **30**, 209 (1887).

[3] W. Thomson, *Phil. Mag.*, (4) **42**, 375 (1871).

[4] Tate, *Phil. Mag.*, (4) **27**, 176 (1864); J. L. Morgan, *Z. physik. Chem.*, **63**, 151 (1908); **64**, 170(1908); *J. Am. Chem. Soc.*, *loc. cit* (1913); *loc. cit.* (1914); J. Traube, *Ber.*, **24**, 3074 (1891); S. Motylewksy, *Z. anorg. allgem. Chem.*, **38**, 410 (1903); J. F. Bottomley, *J. Chem. Soc.*, **83**, 1421 (1903); and others.

[5] W. Ramsay and Shields, *loc. cit;* Renard and P. A. Guye, *J. chim. phys.*, **1**, 374 (1903); **5**, 81, 97 (1907); **9**, 505 (1911); *Arch. sci. phys. nat.*, (4) **11**, 449, 537 (1901); R. Lorenz and F. Kaufler, *Ber.*, **41**, 3727 (1908); R. Lorenz, H. Frei and A. Jabs, *Z. physik. Chem.*, **61**, 468 (1908); Von Hevesy and Lorenz, *ibidem*, **74**, 443 (1910); Lorenz and Liebmann, *ibidem*, **83**, 459 (1913); F. M. Jaeger, *Z. anorg. Chem.*, **101**, 13 (1917); F. Grünauer, *Z. anorg. Chem.*, **39**, 390 (1904).

[6] Simon, *Ann. chim. phys.*, (3) **32**, 5 (1851); Cantor, *Ann. Physik*, **47**, 3909 (1892); Feustel, *Drude's Ann. Physik.*, **16**, 61 (1905); Forch, *ibidem*, **17**, 744 (1905); C. E. Linebarger, *Am. J. Sci.*, (4) **2**, 108 (1896); W. H. Whatmough, *Z. physik. Chem.*, **39**, 129 (1902); J. H. Hock, *Sitzb. Akad. Wiss. Wien, Abt. IIa*, **108**, 516 (1899); W. Jäger, *ibidem*, **100**, 245, 493 (1891).

measurement of the maximum pressure in a gas bubble at the end of a capillary tube immersed in the liquid, at the very instant when the bubble bursts. If this method is modified in the manner indicated by Cantor, using a platinum capillary provided with a very sharp edge, it is quite possible to make absolute determinations of χ.

The principle of the method is quite sound if the edge of the capillary is perfectly circular and of razor sharpness, and if the capillary tube is adjusted in a rigorously perpendicular position with reference to the surface of the liquid. It is necessary to know precisely the radius, r, of the capillary at its knife-edge opening, the specific gravity, d, of the liquid at the temperature of observation, and the depth, i, to which the tube is immersed in the liquid. The maximum gas pressure, H, is equal to the manometer reading minus the hydrostatic pressure corresponding to the depth of immersion, i. Evidently this method can give precise results only if the final condition of the gas bubble actually corresponds to a state of equilibrium attained by passing through a series of mere equilibria; in other words the method must be made practically a static one, the final maximum pressure being independent of the special way in which the pressure within the growing gas bubble is gradually increased.

The rise in pressure within the growing gas bubble must be very slow, as only in this way does it seem possible to eliminate all the differences of pressure throughout the long connecting tubes of the apparatus. It is a well-known fact that, if the connecting tubes are relatively long, the adjustment of such small pressure differences requires a considerable time.

If the radius of the capillary is r (in cm.), the specific gravity of the liquid is d and the observed maximum pressure is H (dynes per cm.), then the surface energy χ (in ergs per sq. cm.) is calculated by Cantor's expression:[1]

[1] *loc. cit.* The formula here given is not precisely that deduced by Cantor. The calculation contained an error; but as E. Schrödinger demonstrated, a theoretical inaccuracy is also present (*Ann. Physik*, 46, 413 (1915)) which is now eliminated so that the coefficient of the third term becomes $-1/12$, instead of $-1/6$ as Cantor had it and $-1/2$ as in Feustel's equation. As has been pointed out, the third term is of no significance in making the actual measurements.

$$\chi = \frac{rH}{2} - \frac{1}{3}dr^2 - \frac{1}{12}\frac{d^2r^3}{H}.$$

The last two terms of the second member of this equation are so small they usually may be neglected in comparison with the experimental errors, being corrections of the second order. Nevertheless we found that a special correction must be applied to values calculated in this manner, because a not altogether legitimate simplification was made in deducing this relationship theoretically. This correction will be taken up later on.

With this limitation, extended experience in using this method convinces us that in the present form it enables one to obtain reliable results that are reproducible within narrow limits. It has the advantage of continually renewing the surface layer of the liquid, thus eliminating the frequently observed and troublesome phenomenon of alteration in this layer. Furthermore the flow of gas can be regulated at will according to the characters of the different liquids, so that possible oxidation or reduction can be prevented.[1] Under the foregoing precautions the results obtained at 1650° may be regarded as just as accurate as those for ordinary temperatures, provided the liquids have no abnormally high viscosity; for the latter to some extent destroys the reliability of the measurements. The influence of the viscosity will be considered in detail further on.

Of all the sources of error that have to be considered, the determination of the depth of immersion, i, seems to be the most significant. If all other errors are assumed to be cumulative, their total effect upon the reproducibility of the results, even at 1650°, is still within about 1 per cent of the true value of χ, and at lower temperatures is within 0.6 per cent of that value. In the case of many molten salts, where H is very large and the viscosity small, the percentage error appears to be even less, not exceeding 0.4 per cent. For our purpose this degree of accuracy may be considered very satisfactory, in view of the enormous difficulties of making measurements at those extreme tem-

[1] If the gas is neutral and does not react with the liquid, the results will be quite comparable, because experience shows that the differences in χ measured with different gases are vanishingly small as compared with experimental errors.

peratures. It may be doubted whether this degree of accuracy at such high temperatures can be improved upon in the near future; and if it may be possible, it is still doubtful whether we should gain much for the purpose proposed. Experience shows that at these extreme temperatures all compounds are in a state of more or less advanced dissociation; and it can have little significance to express the surface energy χ of such compounds in tenths of an erg, when the uncertainty due to the inevitable admixture of the dissociation products will surely be greater than the correction factors resulting from the increased accuracy in the measurements.

APPARATUS AND EXPERIMENTAL EQUIPMENT

Pure dry nitrogen, free from oxygen, was used in all measurements, because this gas appeared to remain quite

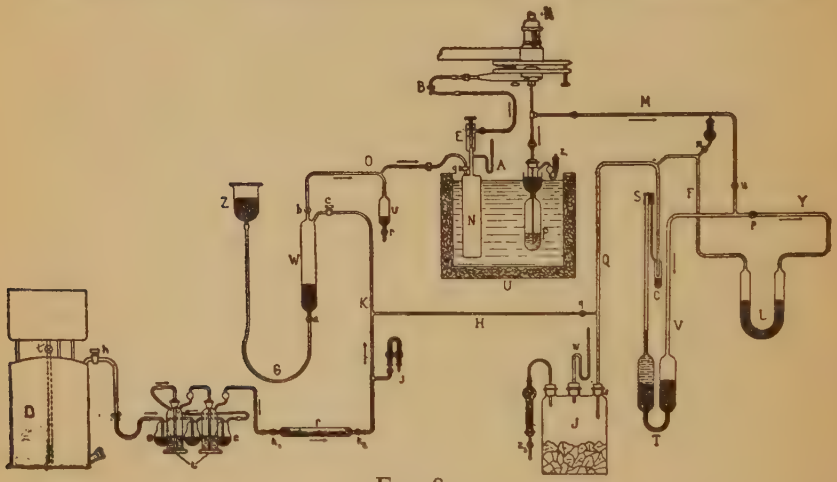


FIG. 89

inert even at the highest temperatures and did not attack either the compounds studied or the thermoelements. Carbon dioxide can be used as a furnace atmosphere up to relatively high temperatures, but it is often rather unsuitable for bubbling through molten salts under such circumstances because of its character as an anhydrous acid. Besides, at the highest temperatures a slight dissociation is always to be feared. Dry nitrogen on the other hand per-

mitted us to drive out the air from the glass bulbs at lower temperatures, and completely prevented the oxidation of the organic liquids investigated.

The nitrogen was prepared from a mixture of pure sodium nitrite and ammonium chloride, washed with distilled water, and collected in the gasometer, *D*, of Figure 89. The gas was led through a series of wash bottles, *e*, filled with an alkaline solution of pyrogallol, and then through others filled with concentrated sulphuric acid (*t*), and finally through the tube, *f*, containing a large surface of freshly sublimed phosphorus pentoxide. The dried gas was stored in a collector, *W*, closed with dry mercury. When needed the nitrogen was pushed out into a metal reservoir, *N*, by means of a movable mercury reservoir, *Z*. Any arbitrarily chosen pressure could be used and was read on the mercury manometer, *A*. The stop-cock, *E*, carries a micrometer used to regulate the current of gas. When studying organic liquids the reservoir, *N*, was placed in the oil-thermostat, *U*, together with the glass bulbs containing the liquid to be investigated. In this way the nitrogen was pre-heated to the temperature of observation, thus preventing disturbances of temperature in the surface layer of the liquid due to small gas bubbles emerging from the capillary tube.

The flow of gas was regulated by the stop-cock, *E*, together with two accurately adjustable pinch-cocks, *B*, inserted between the reservoir, *N*, and the apparatus *R* carrying the capillary tube with its adjustments. By this arrangement one need fear no undesirable cooling of the surface, or any lack of adjustment in the velocity of the gas, both of which are to be avoided as considerable sources of error.

The apparatus *R* (Fig. 96 p. 276) consists of an upright rod *H* about 1 meter high and made of heavily nickeled brass. It rests on a heavy iron tripod fitted with three levelling screws. The vertical rod can be rotated about its axis by means of two sliding disks *O* at the foot of the pillar; these may be clamped fast when desired. This mounting makes it possible to bring the horizontal arm with the adjusting devices and the movable counter weight *I* into any desired

azimuth, and to fix it in position by means of the clamps at *O* and the collar at *H*. A vertical rack and pinion actuated by a crank serves to move the horizontal arm vertically to any position, where it may be fixed by means of clamps: This arm can also be moved horizontally so as to vary its length. In order to prevent a slight bending of the pillar *H*, under certain circumstances, it was found necessary to fasten three steel braces to the iron tripod and to the pillar at *H*. Just above the point *R* the horizontal arm carries a steel support bent at right angles, to which are attached the spiral tubes *G* (Figure 90), of gas-tight aluminum and nearly 3 mm. in diameter, together with their continuation at *U*, where they are coiled in much wider spirals. The ends of the latter are fastened firmly to the horizontal beam built into the laboratory wall just above the whole apparatus. The two sets of spirals seem to be necessary in order to insure the desired mobility of the apparatus with regard to the manometer connections, and also to permit the effective operation of the adjusting devices. On account of the great sensitiveness of the manometer it is necessary to wrap all the connecting tubes of that instrument, as well as the spirals *G* and *U*, in a thick layer of white flannel or asbestos which prevents disturbance due to slight variations of temperature.

The adjusting device *R* is shown on a somewhat larger scale in Figure 90. It is fixed over a resistance furnace and connected with the capillary tube of platinum-rhodium alloy and with the thermoelement *F*. In the drawing the rectangular support with the spirals *G* are also plainly shown together with the hollow water screen *J*, through which a current of cold water is continually circulating. This adjusting device consists of two semicircular parts about 40 cm. in diameter. One part is attached permanently to the apparatus *R*; the other part can be fitted to it by means of pins and short tubes. This latter part also has a circular glass window in which is mounted the movable totally reflecting prism *E* mounted on a horizontal axis. This prism permits one to observe the behavior of the liquid in the furnace, which can be controlled at every instant.

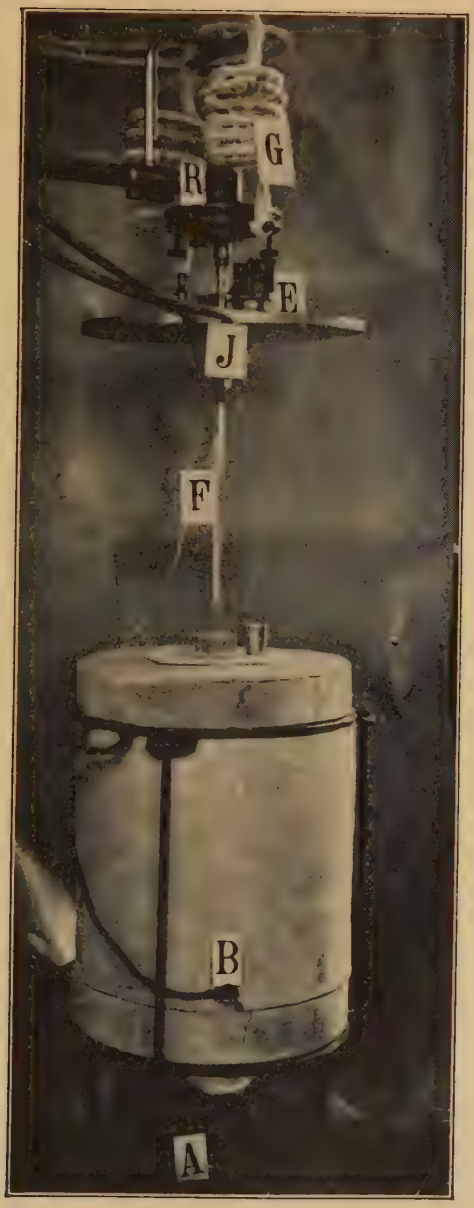


Fig. 90

For temperatures above 1000° green-colored glasses are inserted in front of the prism.

Under the protection of the water screen J, it has proved possible to use the manometer even at temperatures of 1650° without any disturbance due to the heat from the furnace. The furnace B is a platinum, or nickel-chrome, resistance furnace of the usual type. It has an inside-wound heating coil and, when fitted with a central internal tube of alundum, can be heated up to 1400° while without such a central tube it can be raised to about 1650°. The platinum crucible is carried on a movable support of burned magnesite which can be fastened to the iron support A at any height.

Construction and arrangement of the part R of the adjusting device is explained in more detail in Figure 91 where 91B shows an external side view, while a section through the part in a plane perpendicular to that of B is shown by Figure 91A.

The apparatus consists of two metal disks P_1 and P_2; the disk P_2 carrying the tube S can be moved vertically about the knob Q and can be brought into any inclined position with respect to P_1 by means of the set screws A_1 and A_2. If P_2 is turned horizontally the screws A_1 and A_2 together with the springs F_1 and F_2 will slide along the upper disk P_1, the whole upper part thus remaining in its original position. In order to adjust the capillary tube a third screw B was added. To make the adjustment, B is run out of contact with P_1, and after P_1 and P_2 have been brought into the desired relative positions the screw B is turned up until it touches the disk P_1 slightly; thus the two plates are perfectly fixed in their relative positions. Two other tubes S and Y (not shown in Fig. 91B) are bent upward at right angles and attached to the spirals G (Fig. 90). This arrangement sufficiently prevents an undesired movement of the apparatus while the capillary tube is being adjusted, resulting from the influence of the strain and weight of the connecting tubes, while at the same time the micrometer screw M remains in working condition. This micrometer screw M fitted with a drum N and a scale D serves to move the disks P_1 and P_2 together through a known vertical distance. This screw has a pitch of exactly 1 mm. and the cir-

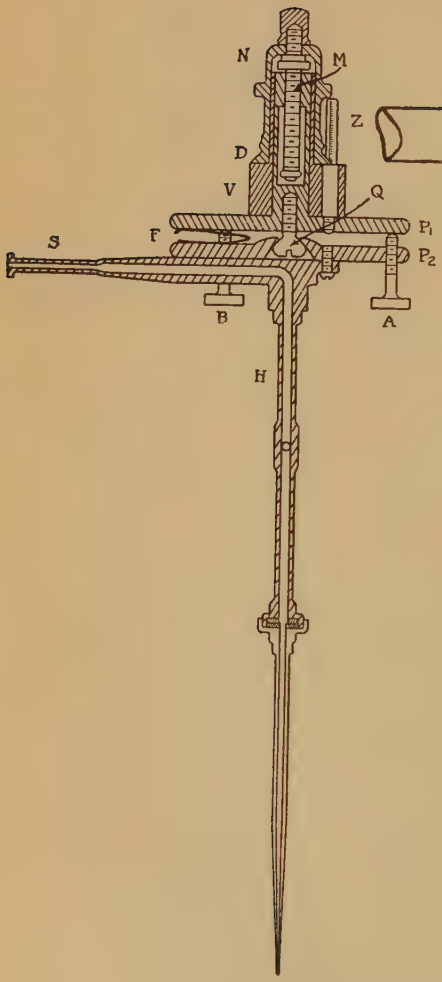


FIG. 91A

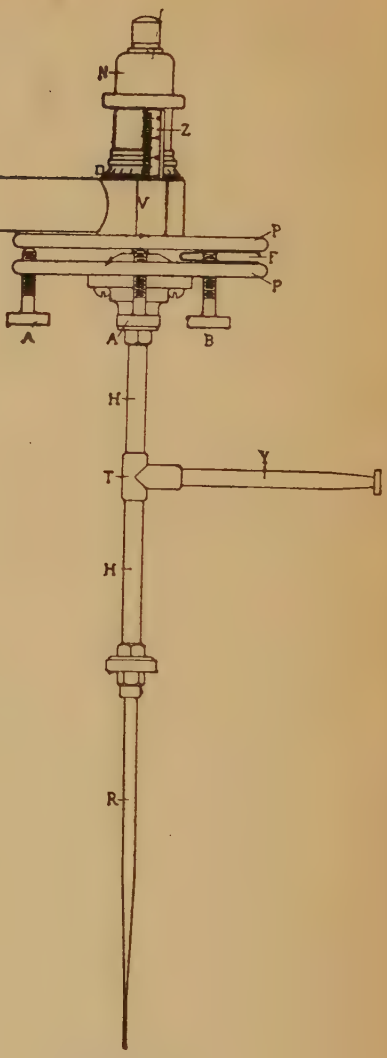


FIG. 91B

cumference of the head is divided into 100 equal parts, thus permitting the measurement of a vertical motion of 0.01 mm. on scale D. This is more than sufficient accuracy, because experience shows that the capillary tube cannot be adjusted in contact with the surface of the liquid with an accuracy greater than about 0.1 mm. During this vertical adjustment the drum N and the micrometer screw M remain in their original positions, because they can move only horizontally about the fixed part V of the apparatus. A vertical scale Z provided with subdivisions for about 30 mm. moves with the two disks P_1 and P_2, permitting the direct reading of the number of revolutions of N. The adjustment of the capillary tube to the surface of the liquid can be made either visually or with the aid of the manometer readings.

Experience soon showed that the slight differences of pressure through the long connecting tubes adjusted themselves so slowly that considerable errors in measurement were sure to occur. Therefore the original equipment of capillary tubes was replaced by 5 mm. gas-tight tubes in part of lead and in part of aluminum. Wherever necessary they were wrapped with a thick layer of asbestos. It required considerable time to get all the connections perfect and free of leaks; but when this had been accomplished the manometer indications were so prompt as to be practically instantaneous. After this change there was no further danger of errors from this source.

The tube junctions were of the usual high-pressure type; and appeared to remain gas-tight even after long use.

For measuring the maximum pressures obtained, we used an instrument built on the principle of the two-liquid manometer. In measuring organic liquids it was necessary to avoid any contamination of the connecting tubes by the vapor of the manometer liquid, so that only pure mercury could serve as one of the liquids in the manometer. For the second liquid we selected normal octane. This liquid is very thin, behaves very well in contact with glass walls and, if the mercury surface is perfectly dry, appears not to blacken the same even after long exposure. The vapor pressure at 20° is only 10.45 mm., the viscosity

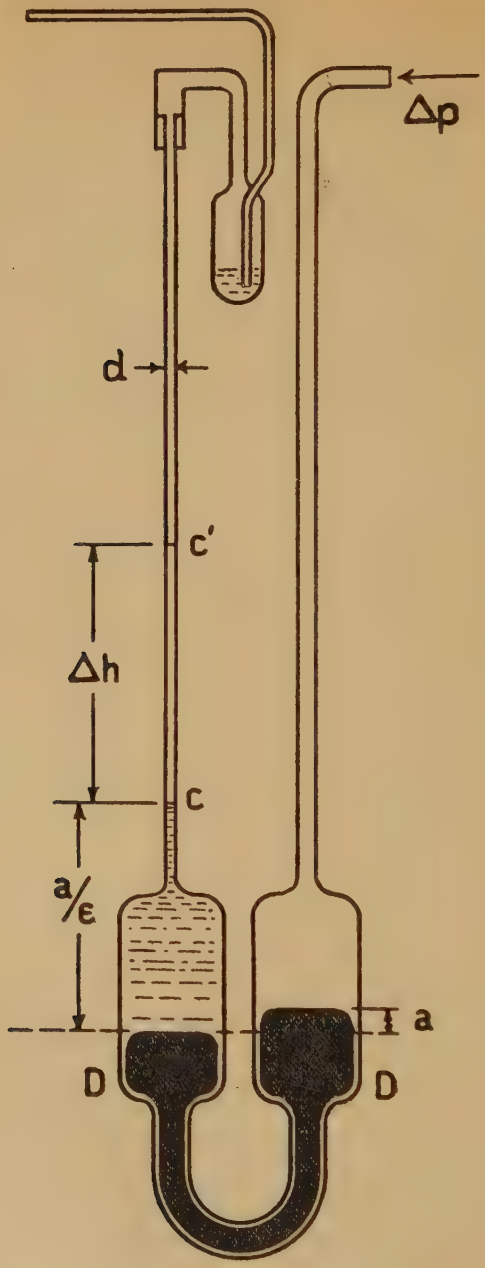


FIG. 92

at 23° is 0.0052 C.G.S., the surface tension at 25° is 21.3 ergs per sq. cm. and the coefficient of expansion is 0.00118. After repeated fractional distillation the boiling point of normal octane was found to be 125° at 758 mm. pressure, and its specific gravity at 25° was $d_{4^\circ} = 0.6985$ or about 19.38 times less than that of mercury.

If the diameter of the wide tube (Figure 92) is D, of the capillary tube is d, and the mercury meniscus on the right is a mm. higher than on the left: then the height c of the octane column on the left side is a/ϵ mm., if $\epsilon = 1/19.28 = 0.0516$. Let Δp be the increase of pressure in mm. of mercury on the right-hand side necessary to depress the mercury surface exactly 1 mm. Then the mercury surface on the left-hand side will rise exactly 1 mm. and the octane column will rise from c to c' ($= \Delta h$ mm.), through D/d mm. The difference in level between the two mercury surfaces is now $(a - 2)$ mm., and the octane column on the left has a height of $(a/\epsilon - 1 + D/d)$ mm. This corresponds to a mercury column of $(a/\epsilon - 1 + D/d)\epsilon = (a - \epsilon + \epsilon D/d)$ mm. Therefore the necessary increase of pressure on the right-hand side ($= \Delta p$) is evidently:

$$(a - \epsilon + \epsilon D/d) - (a - 2)\text{ mm.} = 2 + \epsilon(D/d - 1)\text{ mm.},$$

and thus:

$$\frac{\Delta p}{\Delta h} = \frac{2 + \epsilon\left(\frac{D}{d} - 1\right)}{\frac{D}{d}} = 2\frac{d}{D} + \epsilon\left(1 - \frac{d}{D}\right) = \epsilon + (2 - \epsilon)\frac{d}{D},$$

or:

$$\Delta p = \Delta h\left\{\epsilon + (2 - \epsilon)\frac{d}{D}\right\}$$

The reciprocal of the expression within braces here will be recognized as the multiplication factor, F, of the instrument. For small values of ϵ, $(2 - \epsilon)$ is very nearly 2; therefore it is necessary to reduce d/D as much as possible. In our instrument we met these conditions as follows. Preliminary experiment gave d = 2.406 sq. mm. and D = 1257.36 sq. mm; thus d/D = 0.00191 and F is about 18. Pressure readings seem to be reproducible within 0.1 mm.

of octane, or 0.005 mm. mercury. The accuracy of the measurements was between the limits 0.05 and 0.1 per cent, and therefore more than enough in comparison with the magnitude of the systematic errors of the method.

After many experiments and changes of arrangement the manometer assumed the final form shown in Figure 93, and this is the form in which it was used for all our measurements. The tube *A* is of the best quality of hard glass and connects two bulbs, *B*, about 39.9 mm. in diameter and 130 cu. cm. in volume; their wall-thickness is 1.2 mm. These bulbs must be carefully selected that they may be perfectly cylindrical throughout their full length. Since their height is about 110 mm. it is difficult to find tubes of the desired quality. The capillary tube must have an internal diameter of 1.7–1.8 mm. and walls about 2.5 mm. in thickness, it must be suitable for precise measurements and carefully calibrated. The length is about 600 mm. Another tube *D*, equal in length but about 7 mm. in diameter, serves to connect it with the gas apparatus. The capillary *C* has at its top a silver tube, *E*, slipped over *C*; it communicates with *C* by means of a silver capillary and can be readily removed when necessary. The tube *C* widens at its upper end to about 10 mm. and is joined to the silver tube in such a manner that no dust can contaminate the capillary *C*, while at the lower end it communicates with a small reservoir, *R*, partly filled with octane, the object being to prevent as far as possible any evaporation of the liquid in *C*. For the latter reason also the reservoir, *R*, is placed in the thermostat with the manometer tube. Reservoir *R* communicates with the atmosphere (or the nitrogen) by means of an adjustable glass tube, *G*, which opens into a very wide connection leading to a large three-mouthed flask containing dry calcium oxide, and is also connected with a small manometer, a tube with drying materials, and with the nitrogen reservoir. In Figure 89 the reservoir of octane is indicated by *C*, the silver capillary by *S*, the three-mouthed flask by *J*, the manometer by *w*, the drying tube by z_2, and the connections by *Q* and *H*.

The manometer is placed in a glycerol thermostat (Fig. 93) of the type usual for dilatometer thermostats, but its

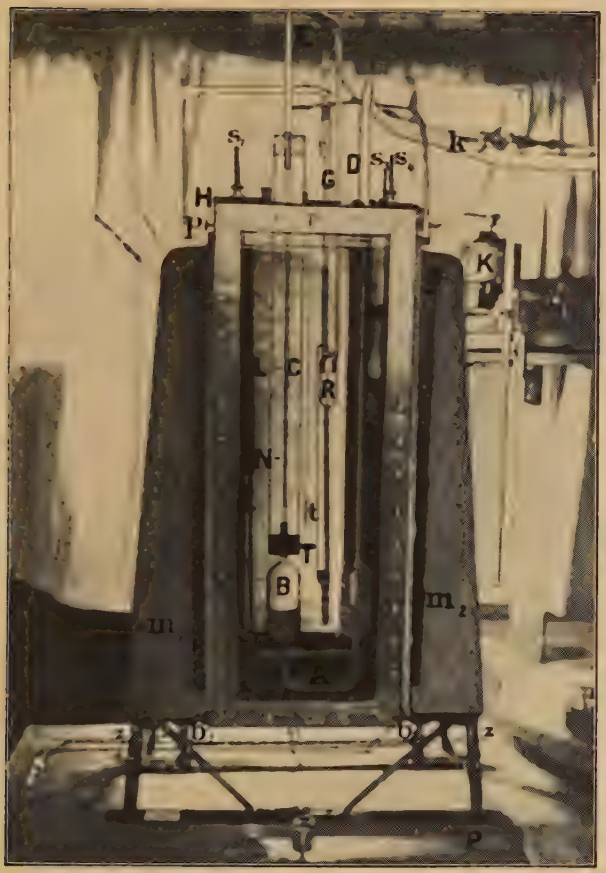


FIG. 93

construction has been altered in some particulars. The thermostats on the market are usually unsuited to our purpose, because they soon develop leaks if these are not originally present; further they are not suited for use with glycerol—chosen on account of its refractive index and low volatility—because it soon dissolves the cement in which the glass windows are set. To overcome these disadvantages two rectangular brass frames about 3 cm. wide were soldered to the thermostat. After smoothing them as perfectly as possible they were given an inside slot, about 5 mm. deep and 1 cm. wide, into which the two glass windows were fastened by means of a layer of very thin rubber cement made by dissolving rubber in carbon disulphide. When the glass windows were finally set, a second coating of this rubber cement was applied and the second brass frame was clamped firmly and uniformly against the first one by means of about 40 screws. The thermostat will hold 22 kg. of glycerol, and shows no leakage after long usage. A pair of small burners, b_1 and b_2, together with a toluene-regulator, T, and a spiral stirrer, M, driven by the motor K, serve to keep the apparatus at a temperature of 25.1° ± 0.1°. This temperature is checked by the thermometer, L, whose scale reads to tenths of a degree. The support, F, is suspended from the lid H by means of four adjustable rods l; and the manometer tube can be adjusted in a strictly vertical position by means of the screws s_1, s_2, s_3, s_4. Just behind the capillary tube C, and within the thermostat, is placed the glass scale N which is accurately divided to 0.2 mm; the scale divisions are lines 3 μ in width and the scale was made by La Compagnie Génévoise. The scale is read by means of a telescope and ocular-micrometer furnished by the same firm, giving an enlargement of about 25 diameters when set up at a distance of about 2 meters. According to the installation that we use, it was necessary to stop the motor K while readings were being made, since even the very slight vibrations thus produced were rather annoying. The thermostat is wrapped in a thick layer of felt, leaving only a narrow opening at the window for the readings. Behind the manometer stands a ground-glass plate illuminated by two long tubular bulbs carrying straight

filaments, each lamp being of 50 candlepower. A water tank with glass windows, placed between the lamps and the thermostat, screens the latter from radiant heat. This lighting method brings out the fine scale divisions and the surface of the octane column very distinctly, without any observable parallax, so that readings of great accuracy can be made against an illuminated background. However, readings closer than 0.1 mm. appeared unnecessary, since the mean variations in the successive determinations of H were about ±0.05 mm. octane, and the total uncertainty is therefore about 0.1 mm. octane pressure or 0.005 mm. mercury.

In using Cantor's or Schrödinger's formula one factor is neglected which, if taken into account, makes a slight but significant correction necessary. The values of χ deduced from H must surely appear somewhat larger than they really are because, in practice, the conditions on which the final relationships between H, d_t, and r of Cantor's theory are based, are not actually completely fulfilled.

We may start with the somewhat briefer derivation of his formula by Feustel.[1] As given in the latter's paper it is evident that Cantor's formula can be valid only in that special case where the angle θ—the angle that the tangent to the sharp edge of the capillary tube from any position on the surface of rotation of the gas bubble, makes with the horizontal surface of the liquid—differs but slightly (ϵ) from 90°; so that $\theta = 90° - \epsilon$, where ϵ has a very small value. Twelve years ago Professor Lorentz was kind enough to draw my attention to the fact that this limiting supposition can be avoided if one makes a few simple substitutions in Feustel's two formulas, viz.,

$$\frac{2\chi}{r}\cos\theta = rd_t\frac{1}{(1-\cos\theta)^2}$$

and

$$\mu = \frac{rd_t\sin\theta}{\cos\theta(1-\cos\theta)^2} + \frac{rd_t}{3\sin\theta}\left(\cos\theta + \frac{2}{1-\cos\theta}\right),$$

[1] R. Feustel, *loc. cit.*

by introducing $q = 2\chi/r^2 d_t$ and $s = \mu/r d_t$, where r is the radius of the capillary tube, and χ and H are as defined above. Making these substitutions, Feustel's formulas can be written

$$q = \frac{1}{4\cos\theta \sin^4 \tfrac{1}{2}\theta}$$

and

$$s = q \sin\theta + \tfrac{1}{3}\left(\cot\theta + \frac{1}{\sin\theta \sin^2 \tfrac{1}{2}\theta}\right)$$

TABLE XV

Corresponding Values of θ, q *and* s.

θ	q	s
0°	∞	∞
10°	4399.4	793.94
20°	292.60	100.080
30°	61.717	30.86
40°	23.850	15.33
45°	16.458	15.21
50°	12.192	12.06
55°	9.588	9.995
60°	8.000	8.660
65°	7.098	7.862
70°	6.753	7.546
70° 31′ 43″	6.750	7.542
75°	7.033	7.814
80°	8.433	9.183
85°	13.770	14.479
86°	16.567	17.269
87°	21.277	21.960
88°	30.764	31.448
89°	59.35	60.027
89° 4′	63.44	64.12
90°	∞	∞

The values of s and q can be calculated for a complete series of values of θ, and they can be plotted against each other on rectangular coördinates. If H is measured, and r and d_t are known, s can be calculated for every experiment and the resulting diagram enables us to find immediately

the corresponding value of q (therefore also of χ). Table XV, above, presents the corresponding values of s and q for a series of values of θ lying between 0° and 90°. This table shows that p and q reach a minimum simultaneously for $\theta = 70° 31' 43''$, so that Cantor's formula strictly holds without appreciable error only for values of ϵ between 0° and 0°55′. The corresponding curve departs but slightly from a straight line; however, we found that this departure suffices to make necessary a correction for all values computed by Cantor's formula.

It is now evident in any special case, that the calculation of the results in this way and by means of Cantor's formula, will never cause an appreciable change in the general shape of the μ,T-curves, and hence neither in the deduced values of $\partial\mu/\partial T$. The deviation from a linear relation between s and q, between $\theta = 70° 31' 43''$ and $\theta = 90°$, is so very slight that a deformation of the curves that is of any importance at all, certainly cannot be the result of this error in computations. There will be, however, a parallel shifting of every curve which will diminish the absolute values of χ and μ by a small amount. This latter influence is not without importance, as is shown by the fact that values of χ calculated from the uncorrected formula are one to three per cent higher than those obtained by the corrected formula. Therefore all observed values were always corrected by means of the plotted curve referred to above.

The capillary tube, *R*, was adjusted in a vertical position with the aid of a mercury mirror. The position of the capillary is altered by means of the screws A_1 and A_2 (Fig. 91) until its reflection in the mercury surface is seen to be in a right line with the tube itself; then P_1 and P_2 are fixed in place by the screw *B*. Originally the capillary tube was made of the purest, iridium-free platinum, this was found to be too soft, however, and was replaced by a tube of an alloy containing 10 to 20 per cent of rhodium. No capillary tubes suitable for the present purpose were found on the market, one was therefore made to order by Heraeus. The rough article with its widened (6 mm) upper end having been delivered, we turned on a lathe the lower conical

end, bringing it to a sharp edge that was further whetted with an oilstone when necessary.

The cross-section was determined by means of a horizontal microscope provided with a moveable-crosshair micrometer having a divided cylinder. The diameter was measured in ten or twelve directions, the squares of these measurements added, the total divided by the number of measurements, and the square root of the quotient was taken as the true value of $2r$. Since the actual observations were being made at extreme temperatures and since it seemed necessary to re-whet the capillary tubes after almost every set of measurements, we used no tubes that had a bore less than 0.040 cm.

The platinum-rhodium capillary tube terminates above in a carefully smoothed, polished brass disk, which is matched by an exactly similar disk terminating the tube of the adjustment apparatus *R*. A very thin ring of mica serves as a washer between these two terminals, which are screwed together and then drawn tight by means of two steel keys, so that the disks are so tightly pressed together that the joint is gas-tight. This junction seemed to be a very perfect one, and if frequently checked for leakage no error need be feared from this source.

Our temperature measurements were made with calibrated thermocouples and the compensator equipment, in the manner always followed by this laboratory. The original plan was to connect the platinum wire of the thermocouple directly to the platinum-rhodium tube, by fusing in the oxygen-blowpipe flame; the tube could then be treated as the positive end of the resultant thermocouple. The perfect insulation of the tube at very high temperatures seemed to present serious obstacles, however, and this plan was abandoned. We adopted the usual thermocouples, provided with insulating Marquardt-capillaries, fixing the thermocouples to the platinum-rhodium tube by means of fine platinum wires. The other end of the thermocouple was connected with the ice-box *Y* (Fig. 96). The wires of the element are bare for about 5 cm. from the junction, which lies in the same horizontal plane as the lower end of the capillary tube and thus is in the immediate vicinity of its

opening. Of course all platinum parts within the furnace (crucibles, coils, etc.) must be made of iridium-free platinum, to prevent as far as possible any contamination of the thermocouple.

The capillary tube is adjusted to the surface of the liquid under investigation in the following manner. The surface of the liquid is strongly illuminated; as the capillary tube is screwed downward, very attentive watch is kept for the instant when the tube end makes contact with its reflection in the surface of the liquid. When the temperatures are above 500° it is not usually necessary, and at temperatures above 1000° it is never necessary, to provide a special illumination for the liquid surface, because at those temperatures the liquid radiates sufficient light to make the observation of the instant of contact very accurate. When the temperature reaches 1400° or higher it often is no longer possible to distinguish the end of the capillary tube from its surroundings, and in these cases the adjustment must be made with the aid of the manometer as described below.

The visual method of setting involves an uncertainty, even after considerable practice, of about 0.1 mm. in the case of organic liquids, corresponding to 0.006–0.008 mm. mercury in the determination of the maximum pressure H. The resulting percentage error of observation is 0.4–0.7; in fact this uncertainty in adjusting the capillary tube to the surface of the liquid appears to be the chief source of error and it is very difficult, if at all possible, to avoid it. However at the higher temperatures and in the case of molten salts—where H is very large—the accuracy of the method is but very slightly affected by this uncertainty.

The other method of adjustment, with the aid of the manometer, carefully applies a very slow flow of nitrogen, after the capillary tube has been brought very close to the surface of the liquid, then while lowering the capillary tube slowly by means of the micrometer screw the manometer is observed closely and the precise moment noted when there occurs a sudden rise of pressure due to the contact of the tube with the surface of the liquid. In this manner the desired purpose was often attained; but here again the uncertainty of setting seemed to be of the same

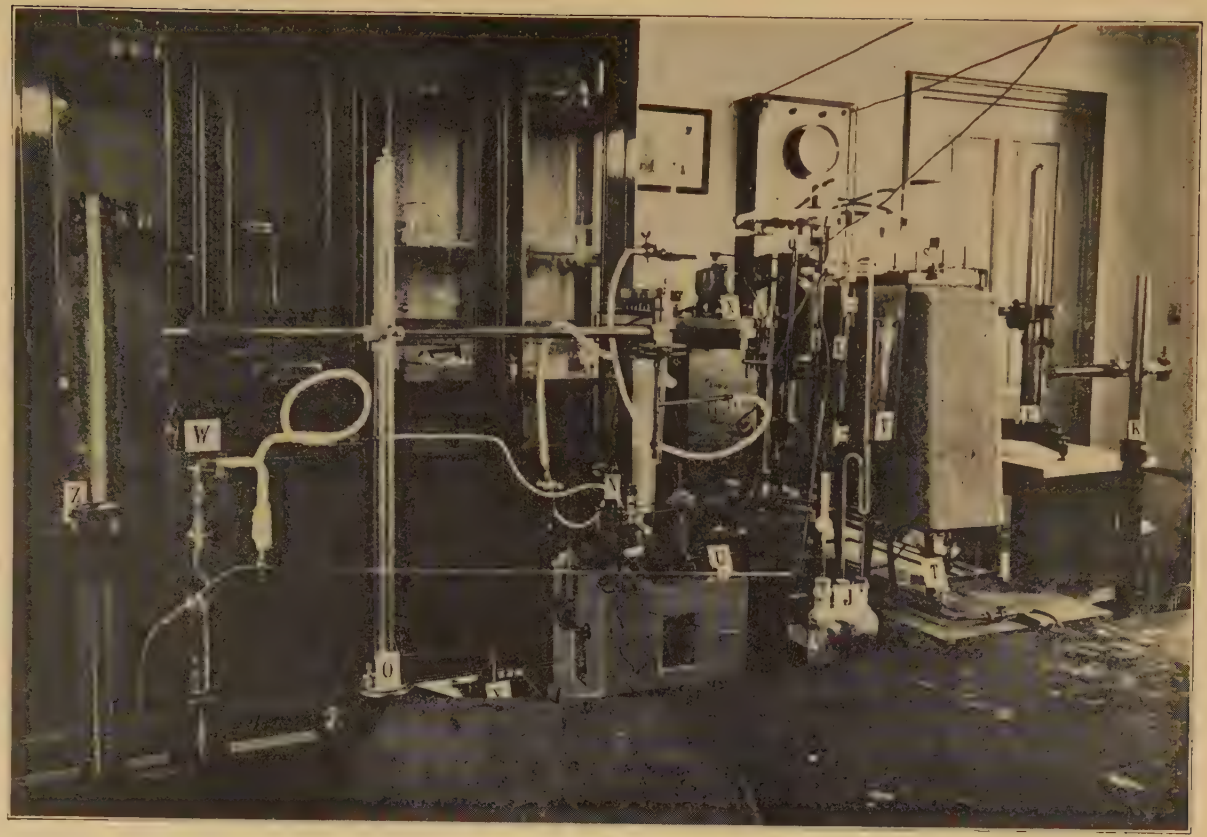


Fig. 95

Apparatus for Measuring Surface Tension of Organic Liquids

order of magnitude as in the case of the visual method. Furthermore it is necessary to make sure that the small column of liquid, which often remains suspended in the capillary when the latter is drawn upward, has no misleading influence on the observation; this thread of liquid must first be expelled by a sufficiently strong flow of nitrogen, before the actual setting on the liquid surface is made in the manner just described.

Our manometer was originally calibrated by a direct comparison with a mercury manometer that was read with the aid of a cathetometer and a divided scale. During the calibration the parallax seemed to be extremely small; the accurate adjustment of the mercury surfaces was greatly facilitated by placing a semi-transparent and diffusely illuminated screen behind the manometer tube; on the screen there were drawn black lines making an angle of about 25° with a horizontal so that their reflections in the mercury surfaces appeared there as a bundle of very fine easily recognized dark lines. After a certain excessive pressure had been applied to both manometers, two observers read both instruments simultaneously; the manometers being connected with each other by a short and very large tube adequately protected against temperature changes.

A long series of determinations showed that a rise of 1 mm. of the octane column was equivalent to an excess pressure of 0.0561 ± 0.0003 mm. mercury (= 74.8 ± 0.4 dynes). After we found that our measurements of χ for pure water were so completely in accord with those by Volkmann, Brünner, Worley, and others, we repeated our calibration—in most cases—by accurately determining χ for pure water at three or more temperatures. The enlargement-factor, F, of the manometer appeared to vary very slowly in all our series of measurements; after a lapse of six months it became 17.91; after a full year it was 17.86; at the end of a year and a half it amounted to 18.10, and so on.

The molten salts to be studied were placed in iridium-free platinum crucibles in most cases; for the organic liquids we used glass vessels of the shape shown in Figure 94. These consisted of a cylindrical glass tube, *P*, having a round bottom and a narrow neck, *A*, with a wider glass

cup, *W*, fused around the neck. A tube, *G*, closed with the stopper *K*, has fixed in it firmly the platinum capillary and carries a side-tube *B* which ends in the drying tube *C*, communicating with the free atmosphere at *Z* and filled with quicklime. The container *P* is cleaned, carefully dried and, if possible, washed out several times with the vapors from the boiling liquid *V*; it is then recharged with a fresh quantity of the liquid *V* and a layer of dry mercury is poured into *W*. The tube is then placed in the oil thermostat, and the capillary with the part *GBC* fixed to it, is then lowered until *G* makes contact with the surface of the mercury. If *V* has reached a constant temperature, the capillary is then lowered further by screwing it down until its point is just in contact with the surface of *V*. The mercury seal insures sufficient freedom of motion while shutting off the liquid *V* from the air,[1] and the small bubbles of nitrogen emerging from *k* are free to escape at *C* and *Z*. All communications with the free air (the connecting tubes of Figure 82) are provided with drying tubes filled with dry calcium oxide.

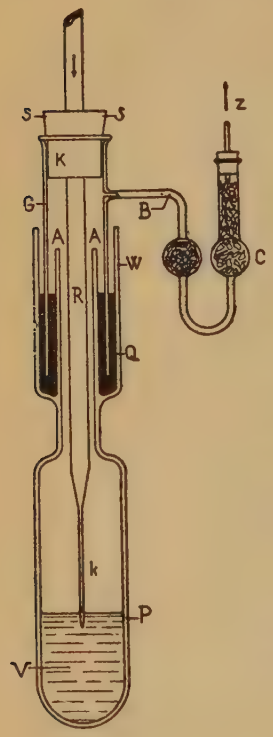


FIG. 94

All measurements were made in such a manner that the zero point was rechecked accurately just before and just after reading the manometer. It is necessary to make sure beforehand that all connections (Figures 95 and 96) are free from leaks, and that a decrease in the speed of the gas flow no longer affects the value of the maximum pressure H. After reaching the highest point of the octane column, the liquid falls suddenly to a point depending upon the

[1] If necessary pure nitrogen may be substituted for the air in the vessel *P*, at the beginning.

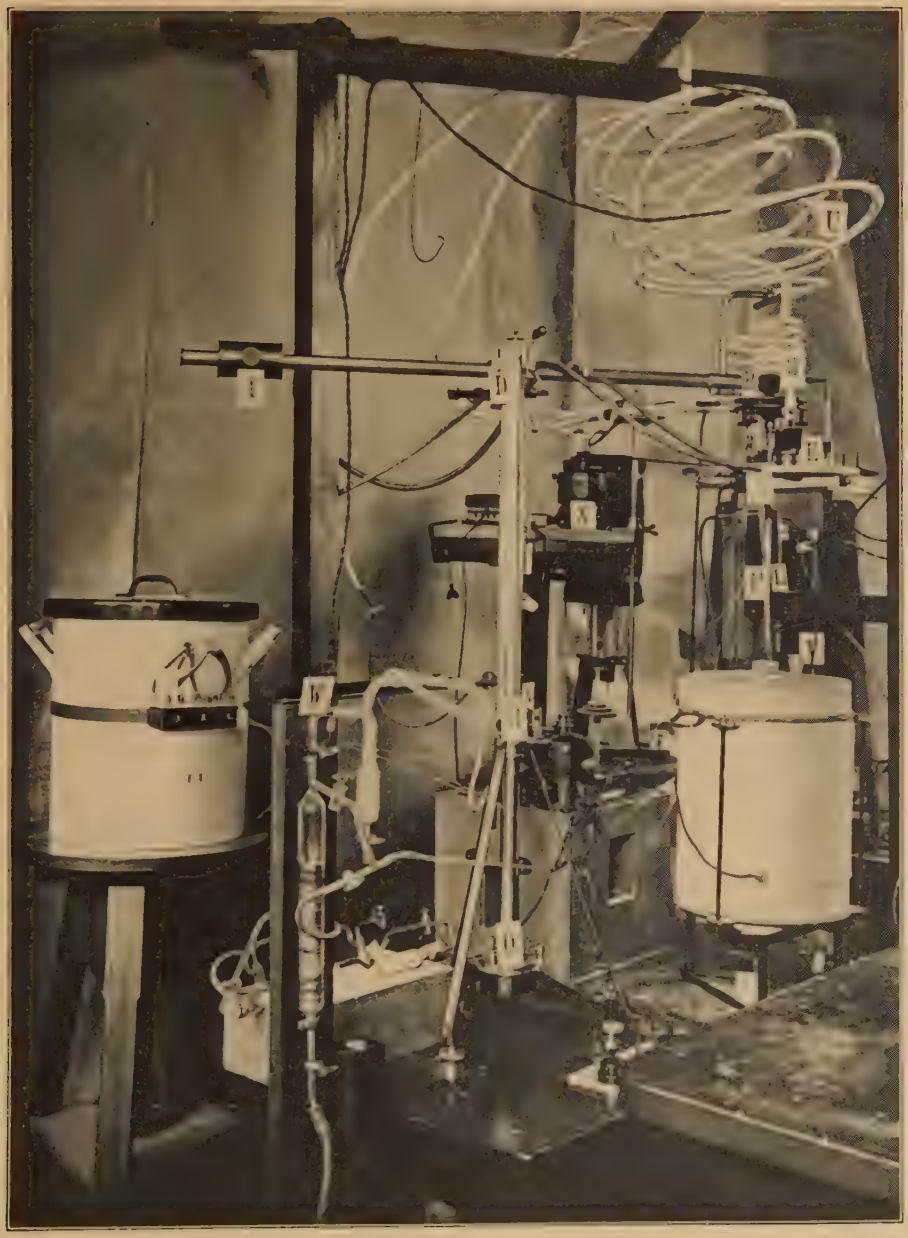


FIG. 96
Apparatus for Measuring Surface Tension of Molten Salts

speed of the flow of gas and then resumes a slow rise. By experience one learns to estimate the reliability of the measurements from the peculiar motion of the octane in the manometer. Finally, the reproducibility of H must be regarded as the decisive criterion for deciding whether or not the true pressure of equilibrium in the gas bubble has been measured. Even when the flow of gas varies within certain limits, the value of H is reproducible quite exactly. The influence of the variation in the depth of immersion, i, on the manometer readings can be determined by repeatedly lowering the capillary tube through known distances as indicated by the micrometer screw *N* (Figure 91), and repeating the readings of the manometer in every case.

In all calculations we took 1333.2 dynes as the equivalent of 1 mm. of mercury at 0°; the surface energy is expressed in ergs per sq. cm.[1]

All our measurements were made with the apparatus that has just been described. They extended over some two hundred organic liquids and fifty molten salts. The next chapter will expound the method for determining the specific gravity of molten salts at high temperatures and then discuss a number of the results obtained.

[1] The numerical expression remains the same whether in dynes per cm. or ergs per sq. cm.

CHAPTER XVI

Specific Gravity and Viscosity Determinations

In order to calculate the corrections for the manometer readings arising from the depth of immersion, i, of the capillary tube and for the term $v^{\frac{2}{3}}$ in the formula for the molecular free surface energy, μ, it is necessary to know exactly the density, d_t, of the liquid at a series of temperatures. By means of such data one can deduce an empirical formula giving v as a function of the temperature, from which one can calculate d_t for any arbitrarily chosen intermediate temperature t. Since these values also enter into all other determinations, such as electrical conductivity and internal friction, the specific gravity is a very important quantity and must be determined as precisely as possible by a reliable method.

In the case of organic liquids at ordinary temperatures we used a pycnometric method, at very low temperatures a volumetric method was used instead. The measurements by these methods were of the usual kinds and are sufficiently described in a previous paper.[1]

In the case of molten salts it was necessary to use a hydrostatic method in which we determined the loss of weight of a platinum double-cone when it was immersed in the molten salt at different temperatures. For this work the set-up was as shown in Figure 97. To a hook on the bottom of one scale pan of a sensitive analytical balance, was attached a fine platinum wire. This wire must have a diameter of at least 0.3 or 0.4 mm. when working at temperatures of 1600°, because above 1500° platinum becomes so soft that a thinner wire would certainly break. This wire, having a length of about 80 cm., passes through a small hole in the floor of the case and a corresponding one in the supporting board, *B*, and finally through the central

[1] F. M. Jaeger, *Z. anorg. Chem.*, **101**, 49 (1917).

opening of the double-walled water-screen, *S*, through which a continuous stream of cold water is flowing. At the free end of the wire is suspended a pure platinum double-cone weighing about 12.17 gm. The balance can be shifted upward or downward by means of the steel cable, *d*, which is wound about a drum turned by means of the crank and gear wheel, *H*. The balance case support, *P*, carries at its lower end a small pulley, *m*, and the balance case itself

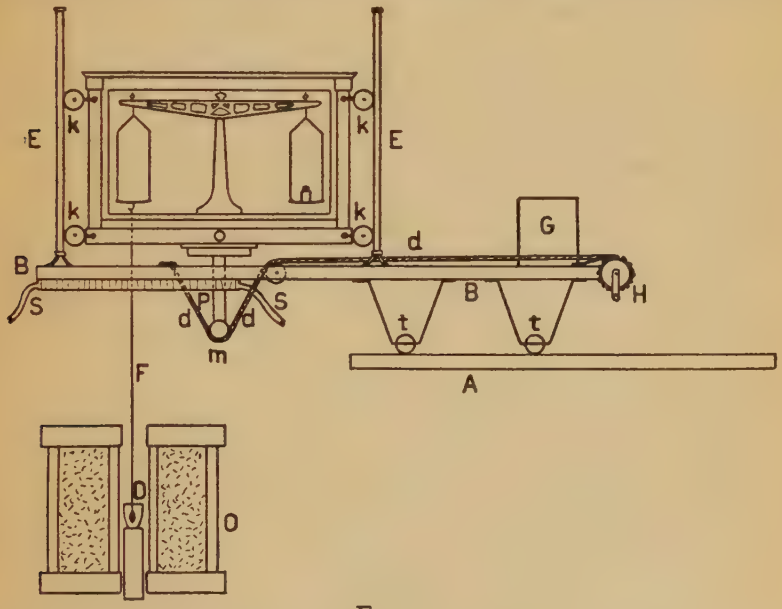


Fig. 97

glides along the four vertical iron guides, *E*, by means of the brass wheels, *k*. The whole apparatus and its support, *B*, can be shifted horizontally, running on four wheels, *t*, that move along the parallel rails *A*. A counter-weight, *G*, serves to balance the whole instrument. By these arrangements the apparatus can be shifted to bring the platinum wire into the desired position just over the furnace *O*, or withdrawn from above the furnace after completing the measurements. The water-screen, *S*, fastened to the under side of the shelf *B* and moving simultaneously with the latter, completely cuts off from the balance case the heat radiated by the furnace, *O*.

The double-cone *D* suspended freely in the air from the scale pan is brought into equilibrium by adding necessary weights to the other pan; the whole apparatus is then lowered sufficiently to permit the double-cone and a certain length of wire, l, to be immersed in the molten salt, which has already been heated in the platinum crucible in the furnace to the constant temperature t°. The weights in the other pan are now shifted until equilibrium is restored, and this process is repeated while the temperature of the furnace is kept constant for a long time. From the buoyant force thus determined, and the temperature t, one can calculate the density d_t, since the coefficient of expansion and the specific gravity of the platinum cone are both known.[1] The experiment may be repeated for other temperatures by simply altering the temperature of the furnace and maintaining it constant for some time. The accuracy of this method was tested beforehand by trying it on liquids of known density and at several temperatures. The results were found to be in perfect agreement with those obtained by pycnometric measurements, if a small correction for the capillary action of the liquid on the suspension wire, *F*, is applied to them. This correction is proportional to the product obtained by multiplying the immersed portion of the wire by its surface tension χ at t°. For the very thin wires we employed this correction never exceeded 0.0001 gm. per erg (= 0.0001 χl); this correction must be added to the observed values of d_t. The results are accurate to the second decimal place, but the third decimal is uncertain, particularly at higher temperatures. Volatile salts will cause serious difficulties because their vapor condenses upon the colder portions of the suspension wire; so that in these cases the complete determination of d_t is impossible.

[1] The density of the platinum double-cone at 0° was 21.485; at any given temperature, t°, it was $d_t^{Pt} = 21.485/(1 + 0.000026604t + 0.000000003972t^2)$. If P = weight of the platinum double-cone + immersed wire in air, p = the corresponding weight after immersion in the melted salt, then the apparent buoyancy = (P − p), the true buoyancy = (P−p) + 0.0001χl. Therefore $\{(P-p)+0.0001\chi l\} \div P$ = (density of the liquid − density of air)/density of platinum, so that the specific gravity of the liquid L under consideration is computed to be $d_t^L = \dfrac{\{(P-p)+0.0001\chi l\}\, d_t^{Pt}}{P} + 0.0001$. In our experiments the value of P was usually about 12.1772.

Although the data obtained in this way are not as precise as were expected, they are the best to be obtained at present under prevailing conditions.

It is probably unnecessary to remark that all substances used in investigations of this kind must be absolutely pure; and, above, all free from any trace of humidity because the presence of water has an enormous influence on the surface tension, particularly in the case of organic liquids.

Regarding the liquids we used, the following general remarks are appropriate. No commercial product, not even the purest obtainable, can be regarded as suitable for this kind of research. The small traces of humidity alone, always contained by even the best chemicals, suffice to invalidate the results. Most of the commercial organic liquids, however, seem to contain several impurities with small or even larger amounts of water. In our work we often secured a preliminary purification by distilling off a small fraction at a boiling point kept constant within one or two degrees. In several cases even this preliminary purification seemed to be impracticable; and in such cases the preparation was dried for a number of days by means of anhydrous sodium sulphate. Then, if the special character of the compound did not forbid it, the material was dried again for a long time by means of freshly sublimed phosphorus pentoxide, after which fractional distillation was tried again. It was now usually possible to separate a fraction whose boiling point remained constant within one or two degrees. Some preparations were successfully dried by means of metallic sodium; and then after very dry fractions, boiling within a few degrees, had been obtained in this way, they were redistilled over a very small flame or on the water bath, under atmospheric or reduced pressures (12–20 mm.). In this latter operation only that fraction boiling within an interval of one degree was used for further treatment. After cooling the liquid for several hours in a closed vessel, either by a salt-ice mixture or by a solid CO_2-alcohol bath, if it crystallized further purification was often possible by repeated freezing and decanting. Often a very thin layer of solid (sometimes ice) was deposited on the walls of the vessel, the remainder being liquid and transparent. The

liquid portion was then poured off into a dry clean vessel and the operation repeated until a solid layer no longer formed. If the solid did continue to appear, the liquid was again treated with fresh phosphorus pentoxide for at least a week, when the freezing and decanting operation was repeated many times. The purified liquid finally was distilled once more at atmospheric or reduced pressure; only the fraction boiling within half a degree was then collected for the purpose of our measurements. It is hardly necessary to state that hygroscopic liquids were preserved and treated in a suitable manner.

The liquid thus obtained usually amounted to a very small fraction, 10 or 20 per cent, of the original immersion preparation. It must be stated that the observed boiling points often differed appreciably from those given in the literature, and in several cases appeared to be lower than the latter, perhaps because in the distillations described in the literature the liquid was heated too rapidly. In our experiments the rate of distillation was often not more than six drops per minute; in some cases, as with toluene, it was impossible to distill from the commercial product a fraction that fulfilled all our conditions. We then had to prepare the substance in some other way, *e.g.* toluene by dry distillation of purified calcium phenylacetate. In the series of compounds described, several were taken from the collection of scientific preparations belonging to the Laboratory of the University of Groningen; from these also only the small fraction of constant boiling point was used for our work.

In spite of the by no means negligible differences in the boiling points observed, in most cases the specific gravities of the liquids differed but very slightly or not at all from the data given in the literature. When the specific gravities agreed as well as this—and they were always checked by pycnometric determinations at 25°—then the specific gravities at other temperatures were calculated from the expansion formula that had sometimes been previously determined. When the direct determination of d_t did not agree with the data in the literature, or if the expansion formula was not known with sufficient accuracy, then we

determined pycnometrically three specific gravities at such temperatures as 25°, 50°, 75° or higher, and from these determinations we calculated an empirical equation of the second degree with respect to T. For our purposes this was quite sufficient, because the specific gravities were all reduced to three decimal places, since densities carried out to a larger number of places would not be worth anything on account of the degree of accuracy of the measurements in our work. With most liquids the average decrease of the specific weight per degree is not far different from 0.001. For temperatures near −70° and above 100° it was often necessary to extrapolate with the aid of established empirical formulas. Although we are aware of the uncertainties that always accompany such extrapolations, we are of the opinion that they did not introduce appreciable errors, since an error in these values could appear only in the third decimal place and the expansion of the liquids goes on so regularly that large errors thus become very improbable. Furthermore there was no other way to proceed at the time, without still greater sacrifices in time and labor.

Our experimental results suggest another question: Is it possible to determine the correct values of χ without the inconveniences arising from the viscosity of the liquid under investigation? Since the internal friction of liquids increases rapidly at lower temperatures, and an extreme viscosity of the liquid causes the maximum pressure H to appear too large, as has been pointed out—even if the gas is bubbled very slowly indeed—this viscosity might be blamed for such deformations of the χ,T-curves as were observed in those cases where they showed a slightly steeper temperature gradient at the lower than at the higher temperatures.

It may be remarked, in the first place, that even in those cases where the observed curvature of the χ,T-curves might suggest such an explanation, nevertheless the curvature often seems not to be parallel with the variations of the viscosity with temperature. This was very striking in the case of those substances where the curvature is so slight that the curves could be regarded as straight lines.

Such curves are characteristic of ethyl benzoate whose viscosity at 10° is about six times that of acetone and drops to two or three times that value over a temperature interval of fifty degrees; isobutylbromide whose χ,T-curve between 0° and 85° can be regarded as a straight line, the viscosity decreasing to less than half its original value—from 0.008 C. G. S. to 0.003 C. G. S. Nor does the χ,T-curve seem to be directly connected with the absolute value of the viscosity in the case of acetic acid whose viscosity is about 3 times, salicylic aldehyde which is 4 times, pyridine, twice, and phenetole where it is about 3 times as large as that of ethyl alcohol. In all these cases the curvature of the χ,T-curves is less than that for ethyl alcohol, all of them being nearly straight lines. In the case of aniline and nitrobenzene, the viscosities being 8 to 10 times as high as that of ethyl formate, the curves are even slightly convex. These curves often showed a more rapid and steeper curvature at higher temperatures, where the viscosity is less; while the portion of the curve between −79° and 0°, corresponding to a region where the viscosity is most variable, is frequently almost a straight line. The viscosity for ethyl alcohol is about three times that of ethyl acetate or ethyl formate, nevertheless the χ,T-curves show about the same curvature in all three cases.

We have met numerous cases in the course of our experiments where it was very clearly impossible to determine the surface energy independently of viscosity, but these cases occurred only where the viscosity attains such enormous magnitude that the liquid became vitreous or gelatinous and moved little or not at all when the vessel was inverted. Such cases were, for example, methyl cyanoacetate, methyl methylacetoacetate, diethyl bromomalonate, diethyl benzylethylmalonate; undercooled dimethyl and diethyl tartrate and α-campholenic acid, and particularly with salol, resorcinemonomethyl- or dimethylethers.

Even in these unfavorable cases we sometimes made good determinations; but in most cases this appears to be impossible, as is shown by the fact that even with so small a gas velocity as 50 to more than 200 seconds for the bubble formation, it proved impossible to determine a maximum pressure, H, that is actually independent of the rate of flow of the gas.

The behavior of such extremely viscous liquids, with respect to the gas bubbles produced in them, is very variable and often quite peculiar. In one case the bubbles are barely detached from the capillary tube, in another case

the gas pressure shows periodical increases and decreases, yet the bubble does not burst; in the third case there is produced a very large bubble that suddenly explodes into a great number of very small bubbles. In no case, however, can one determine a maximum pressure that is really independent of the rate of flow of the gas, and therefore corresponds to a true condition of equilibrium in the gas bubble. The latter fact is characteristic of all our other determinations: the speed of the flow of nitrogen may be varied within rather wide limits, when working with ordinary liquids, without producing a measurable change in the pressure H. On the other hand, when studying a long series of very thin liquids, such as ethyl alcohol, diethyl ether, ethyl formate, ethyl chloroformate, acetone, methylpropylacetone, chloroform, and the like, cooled to $-80°$, we obtained very reliable values of H in spite of the low temperature. That the temperature is occasionally so low, therefore, may not be regarded as of much importance in connection with the abnormally high values of χ and μ sometimes observed. Eötvös' relation is no longer to be regarded as valid at temperatures lower than about half the absolute critical temperature θ_0 of the liquids studied.

When the liquids are of high volatility, and therefore show very considerable vapor pressure at higher temperatures, there is often some difficulty in securing reliable values for H, this maximum pressure being somewhat increased apparently. The right value may be deduced in such cases, however, by frequent readjustments of the capillary until a truly reproducible value is found. These abnormally high vapor pressures cannot be of essential significant influence if the measurements are made accurately and carefully repeated many times.

All in all, we think it quite improbable that the viscosity changes of the liquids studied are properly regarded as the chief cause of the observed curvatures of the χ,T- or μ,T-curves. In cases of abnormally high values of the viscosity, there is no doubt that it seems impossible to determine them precisely by this method; however, in the case of liquids whose viscosity is close to or perhaps a little greater than that of glycerol, for example, such measure-

ments are quite reliable if the formation of the gas bubbles takes place extremely slowly.

Before proceeding to take up the relationships between chemical composition and the coëfficients $\partial\chi/\partial T$ and $\partial\mu/\partial T$, for either organic liquids or molten salts, we must say something about the very general results obtained.

In the first place it is proved, once again, that the free surface energy of liquids—including the particular case of electrically-conducting molten salts studied at very high temperatures—always decreases as the temperature rises.

This fact, to which no exception has ever been found within the temperature range so far studied, is certainly in every respect in perfect accord with views concerning the origin of the surface tensions. It is directly related to the other fact, that a decrease in the molecular surface-layer is accompanied by the evolution of heat, while an increase in the layer connotes an absorption of heat if the temperature remains constant. Further, this gradual decrease in χ as the temperature increases, is certainly in full agreement—at least in the case of the organic liquids—with the continual equalization of the difference in properties between the liquid phase and its coëxistent vapor phase, when the temperature is gradually rising; χ must have been zero at the critical temperature.

For our present purposes the following results are more important:

(1). There seems to be no general linear relationship between χ or μ and T. Observations prove that all three of the conceivable principal species of μ,T-curves (Figure 98) are possible: type 1, concave toward the temperature axis; type 3, convex toward that axis; and type 2, the rectilinear type. There are also some rare cases showing combinations of these three types. It is characteristic of type 1 that $\partial\chi/\partial T$ increases with rising temperature, while it decreases under the same circumstances for curves of type 3; the quotient remains actually constant only in the case of type 2. It is important to notice here that, contrary to prevailing views, the presence of type 2 on one side and of types 1 and 3 on the other side appears to stand in no

clear connection with the absolute values of the quotient $\partial\mu/\partial T$, nor with the absolute values of χ or μ themselves. (2). It appears to be possible to make some arbitrary kind of division of the liquids studied into two principal groups with respect to the value of $\partial\mu/\partial T$. In the first group, A, belong all liquids whose quotient $\partial\mu/\partial T$ really approach

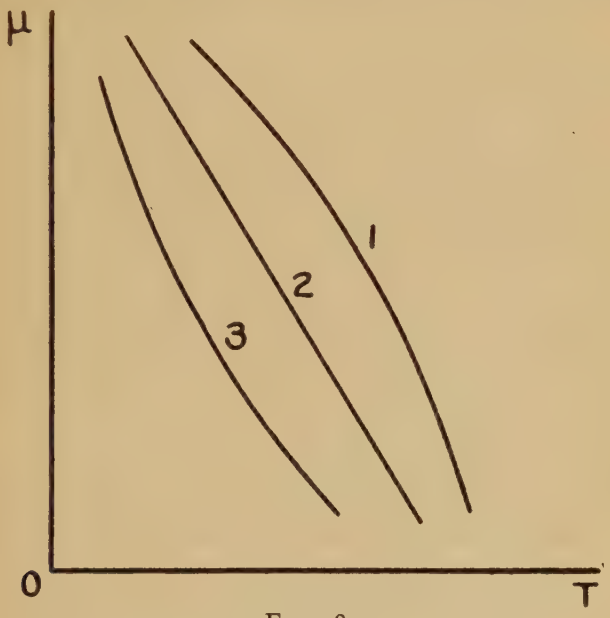


Fig. 98

very nearly Eötvös' "constant" of 2.24 ergs per degree. It must be said, however, that it is evidently only the mean value of $\partial\mu/\partial T$ that can be considered in these cases and that for a rather restricted temperature interval. As just mentioned under (1), these liquids by no means always show a linear relationship between χ and T, corresponding to type 2, and therefore such a linear relationship may be assumed for only rather short sections of their curves in most cases. To group A belong such compounds as ethyl isobutyrate (2.15), isobutyl isobutyrate (2.18), diethyl oxalate (2.16), diethyl malonate (2.52), diethyl tartrate (2.35), ethylacetoacetate (2.19), chloroform (2.06), dimethylaniline (2.23), phenetole (2.14), anethole (2.25),

methyl benzoate (2.21), ethyl benzoate (2.29), methyl salicylate (2.30), ethyl salicylate (2.23), methyl cinnamate (2.43), α-picoline (2.02) and the like. Most of these and analogous substances show a considerable increase of $\partial\mu/\partial T$ at lower temperatures (type 3), and for many of them a value in the vicinity of 2.27 ergs may be accepted within a very narrow temperature range such as 25°–80°.

Group B includes all liquids whose quotients $\partial\mu/\partial T$ are appreciably lower than 2.27 ergs per degree. This group therefore includes such substances as the following: water (1.04), ethyl alcohol (0.94), propyl alcohol (1.10), isobutyl alcohol (1.10), acetone (1.6), acetic acid (1.3), and pyridine (1.6). In several of these liquids, however, $\partial\mu/\partial T$ increases considerably at the lower temperatures, while on the other hand many liquids of group A having rather normal values of $\partial\mu/\partial T$ between 25° and 80°, have abnormally low values at the higher temperatures. So far as it is possible to draw conclusions in this matter from the rather scanty number of specific-gravity determinations, group B would also include the molten salts of the alkali metals: sodium chloride (0.6), potassium chloride (0.64), and others. Furthermore, the hitherto observed relationships between χ and T in the cases of sodium sulphate, sodium molybdate, sodium tungstate, sodium phosphate, potassium bromide, potassium iodide, potassium phosphate, potassium molybdate and tungstate, and lithium sulphate, lithium metaborate, lithium metasilicate, seem to prove that these salts also will have remarkably small values of $\partial\mu/\partial T$.

The prevailing opinion is that liquids belonging to group B must differ from those of A in being "associated", while those of the latter group would be normal liquids. In the case of those liquids showing an almost linear relationship between χ and T (type 2), the "association-coëfficient" x is then calculated from the expression: $x = \left\{\frac{2.2}{(\partial\mu/\partial T)}\right\}^{\frac{3}{2}}$; while for those cases where such a linear relationship may not be assumed, several other formulas

have been proposed.[1] From what has been said, however, one cannot be quite sure that the calculation of the degree of association is a step in the right direction. Among the substances of group A the greater number belong to those whose μ,T-curves are of types 1 or 3. Furthermore, type 3 may be considered as so far in agreement with the postulates of the theory that, in this case at least, there is a possibility that the curve will approach the T-axis asymptotically in the vicinity of the critical temperature. If, however, it is correct to suppose that a decrease in $\partial\mu/\partial T$ indicates an increasing degree of association, it would be very difficult to understand why the majority of liquids show μ,T-curves of type 3; because the gradual decrease of $\partial\mu/\partial T$ with increasing temperature in such cases compels us to conclude that for most liquids the degree of association would increase with rising temperature. Since by far the greater number of dissociations are accompanied by absorption of heat, the conclusion just mentioned certainly may not be regarded as in accord with the law of mobile equilibrium. In the case of liquids that dissociate to a greater extent at higher temperature one must expect, on the contrary, the change characteristic of type 1. For example, water is such a liquid showing gradual dissociation of complex molecules into simpler ones with increasing temperature, and in its case the μ,T-curve actually has the character of the anticipated type, *i.e.* No. 1. We studied some organic liquids in the same way—diethyl oxalate, ethyl propylacetoacetate, propyl and isobutyl cyanoacetates, *o*-toluidine, *m*-methoxyphenol, *p*-dimethoxybenzene, α-campholenic acid—for which a gradual dissociation or decomposition at higher temperatures could be predicted; and for those also we found a more rapid increase of $\partial\mu/\partial T$, as soon as the temperature of incipient decomposition was exceeded. In contrast to these is the case of acetic acid, for which a gradual depolymerization with increasing temperature has been certainly

[1] According to Van der Waals (*Z. Physik*, 13, 716 (1894)), a relation having the form $\partial\chi/\partial T = A(1 - T/\theta_0)^B$—where B at the critical temperature θ_0 should have the value 3/2, but in practice seems to be about 1.23—would sufficiently represent the relation between χ and T in many cases.

proved, and nevertheless $\partial\mu/\partial T$ remains constant over a wide range of temperature.

In my opinion these facts make it very doubtful whether we should continue to regard the changes in $\partial\mu/\partial T$ with temperature, as directly connected with the degree of association of liquids.

In the first place the variation of $\partial\mu/\partial T$ must depend on the manner in which the specific heat c of a liquid is related to the extent S of the latter's surface layer. In general we shall have a relationship $\partial c/\partial S = -T\frac{\partial^2\chi}{\partial T^2}$ whence it follows, as has been pointed out, that χ is a linear function of T in that case only where c is independent of S. Our measurements, however, seem to require that we shall conclude that $\partial^2\chi/\partial T^2$ is not in general equal to zero and that therefore c must be actually dependent on S. This also proves that the specific heat of the surface layer must be different from that for the remainder of the liquid. Therefore the surface energy cannot be altogether "potential" in nature, but must be in part of "kinetic" origin. However, we cannot forsee how the surface energy will vary with advancing polymerization or depolymerization of the liquid; and the same is true, *mutatis mutandis*, of the dependence of μ on T. At the same time it is worth while to note in this connection, that it is not proper to make any definite statement concerning a high degree of association in the case of molten salts, because the observed values of $\partial\mu/\partial T$ are very small and the μ,T-curves seem to approach the rectilinear type 2 much more closely in these cases. Eötvös' theoretical exposition cannot be applied as a whole to such cases as the present one, where no one can tell *a priori* whether the law of corresponding states will be valid. In fact this is the very problem itself: Will future measurements permit us to draw general conclusions from an analogous relation between temperature-coefficient of the molecular surface energy and the degree of association of such electrolytes? Such conclusions could be regarded as sufficiently justified only if we found certain analogies between the behavior of molten salts and of organic liquids. At the present time we are

very far from being able to give a final judgment on this problem, although later I shall draw your attention to some attempts in this direction.

This is not the place for a detailed review of the many measurements on organic liquids of both the aliphatic and of the aromatic series. The general results concerning the relationship between the molecular free surface energy at the same temperature and the chemical composition of compounds related as substitution derivatives, may be summarized as follows:

1. A comparison of the results shows the general truth, that the values of the molecular surface energy at corresponding temperatures increase in homologous series as we come to the terms of the higher hydrocarbon radicals. Although the quantitative relations are not so strikingly evident it seems to be clear, nevertheless, that within the series the influence of the same increase becomes smaller in this respect as the molecular weight increases. This is a fact that must be regarded as quite comprehensible. In most cases these rules hold quite strongly both for aliphatic and for aromatic hydrocarbon radicals.

2. The substitution of N atoms for C atoms or of negative N-containing radicals for H atoms, is followed by a relatively large increase of molecular surface energy at the same temperatures.

3. The substitution of halogens for hydrogen is accompanied by an intense increase in the molecular surface energy at the same temperatures. Evidently the influence increases with the increasing atomic weight of the halogen introduced.

This is illustrated in Figure 99, for example, where the curve for iodobenzene lies above that for bromobenzene and this again above that for chlorobenzene. A substitution of the H by several halogen atoms has a still stronger augmenting influence, thus the curves for *m*- and *p*-dichlorobenzene (Figure 99) lie above the curve for chlorobenzene, and the curve for *p*-dibromobenzene lies above that for bromobenzene, and so on. In the same figure the curve for *p*-bromofluorobenzene is far below that for *p*-dibromobenzene, agreeing with the much feebler influence

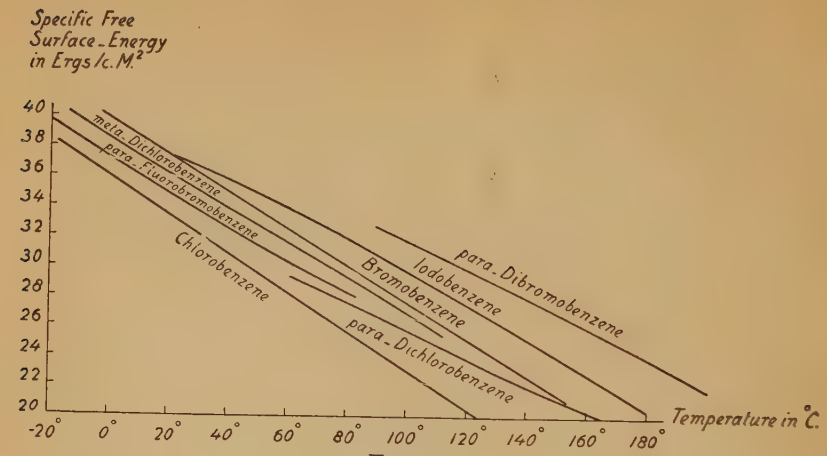


FIG. 99

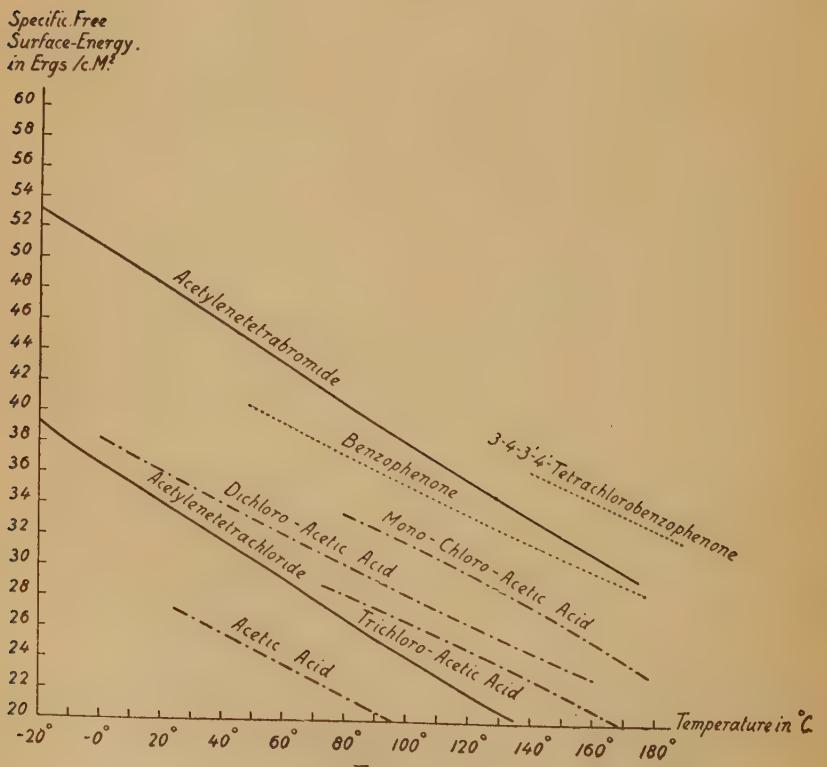


FIG. 100

of the substitution by the fluorine atom as compared with a bromine atom. Again in Figure 100 the curve for 3,4,3′,4′-tetrachlorobenzophenone lies far above the one for benzophenone itself; and that for acetylenetetrabromide is far above that for the tetrachloride. The curve for monochloroacetic acid lies completely above that for acetic acid, and although this is the case also with those for dichloro- and

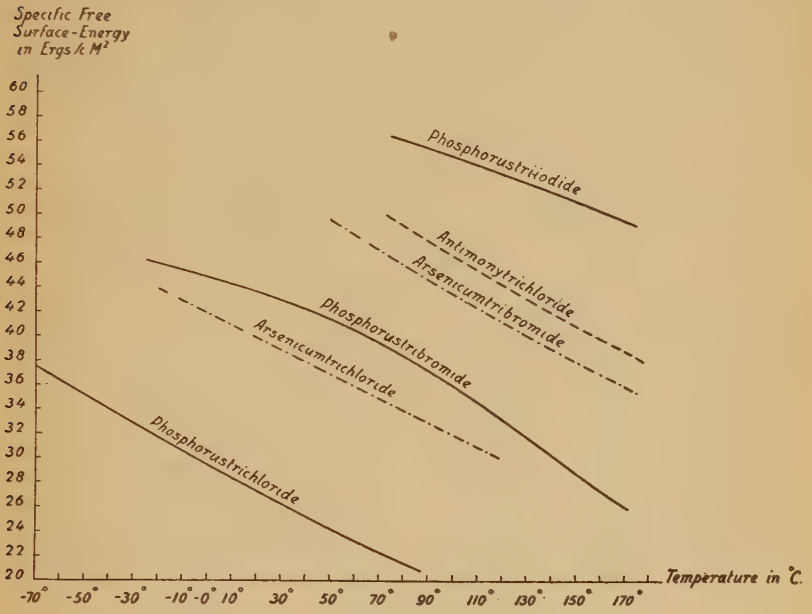


Fig. 101

trichloroacetic acids, the remarkable exception that the two latter lie beneath the curve for monochloroacetic acid calls for a later explanation. It may be pointed out here that similar relationships are found in the case of such inorganic liquids as PCl_3, PBr_3, $AsCl_3$, and $AsBr_3$ (Figure 101). We have to keep these results in mind when comparing the behavior of these liquids with that of the molten salts.

In general, structural as well as position isomerides show quite divergent curves for the relation between molecular or specific surface energy and temperature. Figure 99 shows this for the cases of *m*- and *p*-dichlorobenzenes. In

structural isomerides the values of the surface tension often seem smaller, at the same temperatures, the greater the branching of their chain of carbon atoms.

Having completed this survey, I would now draw your attention in particular to the observed behaviors of inorganic compounds and molten salts. In the course of our investigations we determined the surface tensions, in terms of temperature, of such compounds as S_2Cl_2, PCl_3, PBr_3, PI_3, $AsCl_3$, $AsBr_3$, $SbCl_3$, $BiCl_3$, and $BiBr_3$. We also made similar studies of about fifty molten salts, such as the halogenides of the alkali metals, as well as the nitrates, meta-

TABLE XVI

Type of measurements on molten salts, illustrated by those for Potassium Sulphate, K_2SO_4.

Temperature	Maximum pressure H		Specific surface-tension χ	Sp. Gr. d_4^t°	Molecular surface energy, μ
°C	mm of Hg	Dynes	Ergs/sq. cm.		Ergs/sq.cm.
1070.2	4.080	5439	143.7	1.888	2935
1103	4.048	5397	142.6	1.870	2931
1145	3.989	5318	140.6	1.848	2913
1199	3.878	5171	136.7	1.818	2863
1247	3.762	5016	132.7	1.792	2806
1305.5	3.651	4868	128.8	1.760	2757
1347	3.578	4770	126.2	1.737	2725
1371.5	3.529	4705	124.6	1.724	2704
1400	3.468	4623	122.4	1.709	2672
1439.5	3.393	4523	119.8	1.687	2637
1462.5	3.344	4458	118.1	1.674	2613
1490.4	3.286	4381	116.1	1.660	2584
1530.3	3.228	4304	114.1	1.637	2563
1586	3.130	4173	110.7	1.607	2517
1656	3.020	4026	106.8	1.569	2468

Molecular wt. = 174.27; Radius of capillary = 0.0524 cm.
Depth of immersion = 0.1 mm; Melting point = 1067°; no appreciable dissociation at 1550°. Sp. gr. at $\left\{\begin{matrix}1102.5^\circ = 1.871\\1202.5^\circ = 1.815\\1291^\circ = 1.768\end{matrix}\right\}$ corrected for capillarity on the wire.

In general $d_4^t{}^\circ = 1.872 - 0.0005449(t - 1100)$.

Temperature coefficient $\partial\mu/\partial T$ rather constant, mean = 0.90 ergs per degree, except the very low value in the immediate vicinity of the melting point.

borates, metasilicates, sulphates, molybdates and tungstates of these metals. The two classes of compounds differ principally therein, that those of the first class are derivatives of such metalloid elements as P or S or semi-metalloid amphoteric elements like As and Sb. The element bismuth is more closely related to the true metals and therefore represents to some extent a transitional element between the former and the second group, which are all derivatives of strong, truly electropositive metals.

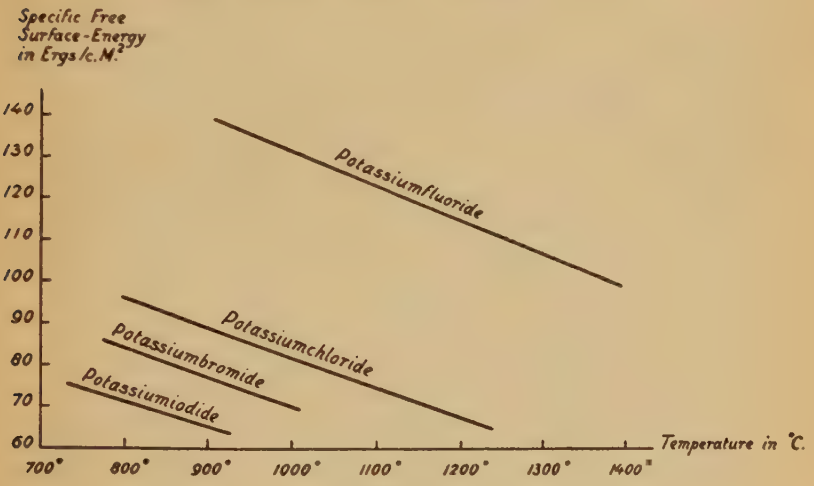


Fig. 102

Table XVI illustrates such a series of measurements with molten salts, by means of the data secured for potassium sulphate, K_2SO_4.

Concerning the halogenides of those elements that we put in our first class, P, As, and the others, it must be said, first, that although the temperature coëfficient $\partial\mu/\partial T$ is generally less than 2.24 ergs per degree, it is appreciably greater than that for the true molten salts in all the cases that we investigated. They behave in a manner that is certainly much more closely related to that of the organic liquids we have mentioned, than to the molten salts of our group 2. There is an undeniable influence of the much lower melting and boiling points of those compounds as compared with corresponding features of the metallic salts.

One encounters here, however, a striking contrast with the facts observed for the true salts, since the influence of the replacement of F by Cl, Br, and I, successively upon the values of the specific surface-tension χ is exactly opposite in the case of the compounds of the first class and of the organic liquids, to what it is for the molten salts. In the case first mentioned, the increase in the specific surface-tension χ follows the increasing atomic weights of the halogens (Figure 101); in the case of the molten alkali-salts, the curves of the specific surface tension for the fluorides are located far above those for the corresponding chlorides, the latter again being above those for the bromides, which in turn stand above those for the iodides (Figures 102 and 103). This fact is repeated without exception in all cases.[1] As may be seen by Figure 104, the substitution of the lighter alkali metal by a heavier one in the molten salts, has the effect of lowering the specific surface tension at the same temperature—a phenomenon that is precisely opposite to what happens in the case of, for example, PCl_3 and $AsCl_3$ or $SbCl_3$.

This radical contrast between the two kinds of compounds is undoubtedly connected with the much stronger electrochemical contrast existing between electronegative halogens and strongly electropositive alkali metals, than that obtaining between the halogens and the elements of the first group. Therefore it is also certainly related to the fact that electrically charged ions are present in the liquid phases of the metallic salt, while they are absent in the organic liquids and either absent or in very much feebler concentration in such liquids as PCl_3, $AsCl_3$, and $AsBr_3$. Certainly the sequence of the curves for the salts of bismuth—which are much nearer to the true metallic salts than are the other compounds of the first class—appears to be reversed here because of the circumstance mentioned. The remarkable exception referred to in the case of dichloro- and trichloroacetic acids undoubtedly is to be

[1] It must be mentioned here in advance that these regular mutual locations of the curves for the χ,T-function do not characterize the μ,T-curves of the same salts, but are present only for the dependency of χ on T.—*See* F. M. Jaeger, *Z. anorg. Chem.*, 101, 202f (1917). The specific surface energy seems to be more closely connected with the chemical constitution of these salts than is the molecular one.

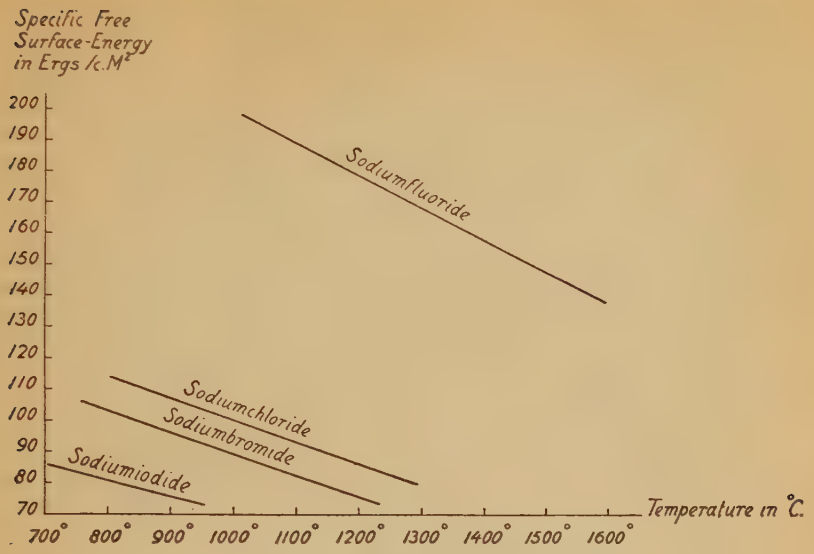


FIG. 103

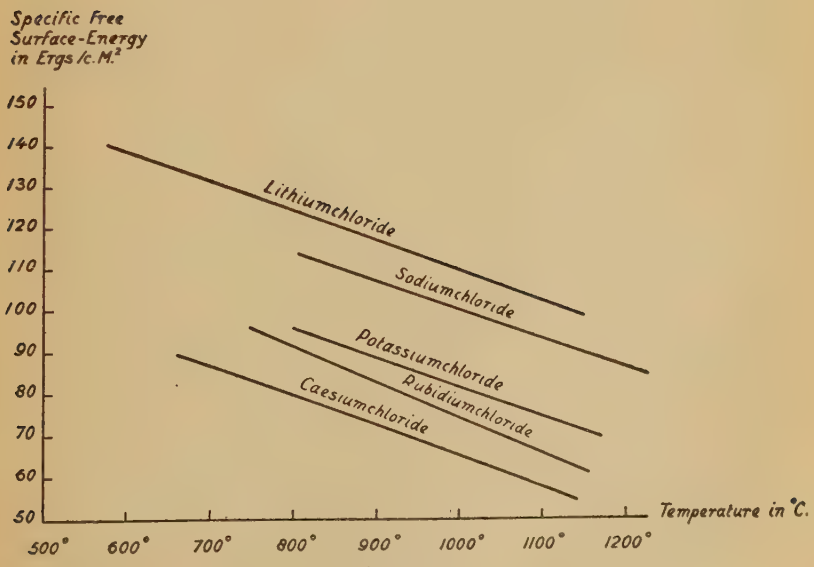


FIG. 104

attributed to the same cause. Here two influences are superimposed: the increase in the surface tension of the acetic acid due to the substitution of the chlorine atoms, and the depressing tendency due to the presence of $H^{\cdot}$ and substituted acid ions, since di- and trichloroacetic acids are both stronger acids than either acetic or monochloroacetic acids.

These facts may indeed be considered in full agreement with the views of Lewis, Langmuir and Kossel concerning the nature of the mutual linkage of atoms in compounds of our first class, as contrasted with that occurring in such strongly ionizing substances as are true metallic salts in the liquid state.

The total surface energy, U_0, of a substance is approximately equal to its free surface energy if extrapolated to absolute zero. This total energy is appreciably a measure of the potential energy of the electromagnetic fields of force surrounding the individual atoms.

In such salts as NaCl and KBr it is assumed, today, that the linkage between the constituent atoms is due to the halogen atoms taking up an electron from the outer electronic shell of the metal, so that the two ions thus formed assume an electronic configuration characteristic of the inert gases neon, argon, krypton, etc. (constituting Langmuir's and Kossel's first mode of linkage). Concerning this, we may say that the electronegative charges of the electrons thus displaced are responsible, in large part, for the energy of the electrostatic fields surrounding the atoms of the liquid considered. It follows from this that the surface energy of molten salts like KCl and NaCl is chiefly determined by the electrostatic energy of the ions present, and according to Coulomb's law the controlling electrostatic forces between them are inversely proportional to the square of their mutual distances. This last condition implies that the greater the "volume" of the ion, the feebler the electrostatic forces will be for each unit of a surface layer filled with such ions, they being perhaps mutually oriented. Therefore, if a salt like KI has, other things being equal, a smaller surface energy than KF, this fact must be regarded as a logical corollary to the other

one, *i.e.* that weaker electrostatic forces exist in the KI surface layer than in the KF surface layer. We meet similar relations in a number of other connections relating to the properties of salts: boiling points, melting points, cohesion, hardness, and the like (Born and others).

However, another portion of the total energy, for both classes of substances here considered, must also be related to the electromagnetic stray fields about the individual atoms, due to the special configuration and distribution of those electrons within their outer electronic shells. The attractive forces induced by this special cause are clearly manifested in, for example, the condensation phenomena of the inert gases. It is now the common opinion that these outer electrons are less firmly held in the atoms of those elements having higher atomic weights, than in the atoms of those others belonging to the same group but of lower atomic weight; so that it is much easier to bring about a change in the arrangement of the outer electrons, by the influence of other surrounding atoms, in the case of the heavier elements than in the case of the lighter ones of their group. The attractive forces originating in these stray fields will therefore become more conspicuous, the higher the atomic weight of the element under consideration; for example, it is easily understood why the tendency to form complex addition compounds among the halogens is much stronger with the iodine derivatives than with the other members of the series. The organic liquids, such as the organic halogen derivatives, and such inorganic compounds as PCl_3, PBr_3, $AsCl_3$, and $AsBr_3$, either are not constructed according to the manner of the ionizing metallic salts considered above or show such a structure only in a subordinate degree. According to modern views, their structure shows that every pair of directly linked atoms share a pair of electrons, thus between a C and a Cl or between a P and a halogen atom. Therefore, in this case the halogen atom itself is almost neutral electrically, so that the surrounding field of force in this case would not be determined by the atomic charge—as was the case in the metallic salts—but by the fact that the unsymmetrical distribution of its electrons in the outer shells gives rise

to stray fields and therefore to the attractive forces they exhibit. Contrary to what happened in the case of the salts discussed above, it is just these forces that now strongly predominate in the case of the compounds of the class here considered. Indeed, the boiling points, heats of vaporization, and the like for these liquids—even with the halogens themselves—will appear higher, the larger the atomic weights of the halogens with which they are compared. The same is true concerning the surface energy of their derivatives, because the attractive forces and the potential energy in their surface layers will now be determined almost exclusively by the existence of electromagnetic stray fields. Many other applications of these views and principles to these and analogous subjects will be found in Langmuir's papers.

Concerning the absolute values of the specific and molecular surface energy, with its temperature coëfficient $\partial\mu/\partial T$, the following remains to be said.

One of the most surprising facts is that, even at very high temperatures, χ and μ are very large for these salts, nevertheless or perhaps precisely on this account, the temperature coëfficient appears to be extremely small.

The absolute values of χ may be represented with sufficient accuracy for the values observed, by the following expression:

$$\chi_t = a - b(t - t_m) + c(t - t_m)^2,$$

where t is temperature, t_m the ordinary melting point, and a, b, and c, have the values given in Table XVII, a evidently being the value of χ at the melting point.

The coëfficient b in Table XVII seems to decrease with the increasing atomic weight of the halogen, when one compares the four halogenides of the same alkali metal. The values of c are practically zero in all cases.

The temperature coefficients $\partial\mu/\partial T$ are very small (see Table XVIII) and vary between 0.3 erg and 1 erg for each degree. Therefore, on the average, they are not less than 3 to 7 times smaller than in the case of normal organic liquids.

TABLE XVII

Melting points and values of a, b, *and* c *for the four Halogenides of Various Metals.*

Salt	Melting point	a	b	c
LiF	840°	255.2	0.126	0
LiCl	608	140.2	0.076	0
NaF	990	201.6	0.106	0
NaCl	801	114.1	0.071	0
NaBr	768	106.5	0.069	0
NaI	660	88.2	0.053	0
KF	858	143.2	0.087	0
KCl	780	97.4	0.072	0
KBr	734	88.8	0.070	0
KI	681	78.3	0.064	0
RbF	765	132.0	0.131	0.00012
RbCl	720	98.3	0.086	0
RbBr	685	90.7	0.069	0
RbI	642	80.3	0.065	0
CsF	692	107.1	0.088	0.00004
CsCl	646	91.3	0.077	0
CsBr	631	83.6	0.063	0
CsI	620	91.6	0.056	0

TABLE XVIII

Values of $\partial\mu/\partial T$ *for the Alkali, Thallous and Stannous halogenides.*

Metals:	Fluoride:	Chloride:	Bromide:	Iodide:
Lithium	0.40–0.58	0.47	——	——
Sodium	0.52	0.48	0.53	0.29–0.63
Potassium	0.33–0.83	0.68	0.76	1.58–0.41
Rubidium	1.0 –0.40	1.02	0.77	0.95
Cesium	0.72–0.36	0.80–1.7	0.90–0.57	0.82
Thallium	——	——	——	——
Tin	——	1.0	——	——

The corresponding values for the sulphates, nitrates, molybdates, tungstates, and metaphosphates of the same metals are given in Table XIX.

TABLE XIX

Values of $\partial\mu/\partial T$ for the Sulphates, Nitrates, Molybdates, Tungstates and Metaphosphates of the Alkali metals, Thallium and Tin.

Metals:	Nitrate:	Molybdate:	Tungstate:	Metaphosphate:	Sulphate
Lithium	0.45	——	——	——	0.50
Sodium	0.24–0.45	1.2–0.56	0.64–0.98	0.43–1.1	0.30
Potassium	0.83	0.79	——	0.91–1.28	0.90
Rubidium	0.78	——	——	——	1.98–0.43
Cesium	1.18–0.42	——	——	——	1.91–0.43
Thallium	0.81	——	——	——	——
Tin	——	——	——	——	——

The values of a, b, and c in the above formula, for the specific surface tensions at t° of these salts, are given in Table XX.

TABLE XX

Values of the coëfficients a, b, *and* c, *for certain Sulphates, Nitrates, Borates, Molybdates and Tungstates, at specific surface tensions at* t°.

Salt	t°	a	b	c
Li_2SO_4	852°	224.4	0.067	0
Na_2SO_4	884	196.3	0.140	0.00042
K_2SO_4	1074	144.5	0.066	0
Rb_2SO_4	1055	135.0	0.087	0.00007
Cs_2SO_4	1015	113.1	0.087	0.00006
$LiNO_3$	254	118.4	0.063	0
$NaNO_3$	312	120.7	0.063	0
KNO_3	339	112.9	0.075	0
$RbNO_3$	304	109.4	0.075	0
$CsNO_3$	414	92.0	0.084	0
$LiBO_2$	845	264.8	0.082	0
$NaBO_2$	965	201.6	0.159	0
KBO_2	946	136.6	0.570	0.00053
Na_2MoO_4	687	215.1	0.121	0.00009
K_2MoO_4	919	152.5	0.066	0
Na_2WO_4	694	204.4	0.068	0
K_2WO_4	921	158.2	0.083	0
$NaPO_3$	620	209.5	0.059	0
KPO_3	820	161.2	0.069	0

Here again the coëfficient c is practically zero, so that it is a safe approximation to the truth to describe the χ,T-curves of molten salts as practically straight lines.

The remarkable fact that the temperature coëfficients of the free molecular surface energy era so very small, led former investigators to assume that molten salts were strongly associated liquids.[1] It is, however, very doubtful whether this conclusion is justified, because, as we have seen, the ideas concerning the degree of association of such liquids are all based upon the validity of Van der Waals' law of corresponding states; and it seems very problematic whether this law really holds for such strong electrolytes as molten salts. If this latter consideration leads to the rejection of the law, then all conclusions deduced from it also fall to the ground. It is worth while to remember that the regularities, mentioned above in connection with the surface tension of molten salts and their chemical composition (see p. 296), relate only to the mutual relations of the χ,T-curves, not to the μ,T-curves. The specific surface energy seems to have a more intrinsic significance for such salts than does the so-called "molecular" surface energy. If the molten salts were completely dissociated liquids and their dissociation coëfficient α therefore equal to 1, both in the interior as well as on the surface layer, the above significance would be quite evident. This characteristic contrast between molten salts and other liquids may be explained in another way also. Walden[2] was the first to draw the attention of chemists to a number of numerical relationships between the values of the following expressions, at the boiling points of various compounds —if these temperatures are, in some way or other, "corresponding" temperatures.

$$Ma_b^2 = \frac{2\chi_b M}{g d_b T_b}, \text{ and } Ma_m^2 = \frac{2\chi_m M}{g d_m T_m},$$

where χ_b, d_b, χ_m, d_m, are the values of χ and d_t at absolute boiling point T_b and the absolute melting point T_m, respectively, and g is the acceleration of gravity.

[1] Lorenz, Liebmann and Hochberg, *Z. anorg. Chem.*, 94, 301 (1916).

[2] Walden, *Z. physik. Chem.*, 65, 257 (1909); *Z. Elektrochem.*, 14, 713 (1908). For the boiling point these deductions are founded upon the assumed validity of Trouton's law: Q_b/T_b = Constant (about 20.7). See p. 255.

If Ma^2 is called the molecular cohesion, Walden emphasizes the fact that at the melting and boiling points of non-associated liquids, the ratio of molecular cohesion to the absolute melting or boiling points, must be practically constant (about 1.156 for b.p., and 3.56 for m.p.). The available data now show that, although these relations are not rigorously true, they are sufficiently correct for organic liquids having a normal value for $\partial\mu/\partial T$, and approximately so for such inorganic liquids as PCl_3, PBr_3, and $AsBr_3$. But at the melting point Ma_m^2/T_m is lower for salts of bismuth and for the true molten salts, with very few exceptions (Na_2MoO_4; Na_2WO), being much smaller than 3.65 as is shown by the data of Table XXI.

In general Ma_m^2/T_m appears to increase with increasing atomic weight of the halogens, in the case of the alkali halogenides, for example:

	Li	Na	K	Rb	Cs
F	0.66	0.70	0.78	1.02	0.96
Cl	0.89	0.81	0.93	1.13	1.20
Br	——	0.92	1.01	1.19	1.27
I	——	1.08	1.13	1.34	1.39

For the other salts here studied there appear to be no such regularities. The singular position of the molten salts among the liquids reinvestigated, is confirmed in this respect also, although there seem to be no indications corroborating the opinion that it is due to a considerable degree of association in these molten salts.

The question as to whether the behavior of molten salts satisfies the postulates of the law of corresponding states, is regarded from another standpoint by some other authors. Lorenz and Herz[1] have tried to find evidence to support the validity of that law in the case of these electrolytes, by deducing numerical relations from the data I obtained in the course of my investigations. Such relations would then be quite analogous to those that are to be expected in the case of ordinary liquids.

[1] R. Lorenz and W. Herz, *Z. anorg. allgem. Chem.*, **117**, 103 (1921). *See also* R. Lorenz, *ibidem*, **94**, 240 (1916); R. Lorenz, and F. Kaufler, *Elektrochemie geschmolzener Salze*, p. 3 (Leipzig, 1909).

TABLE XXI

The Specific Cohesion and Molecular Cohesion at Absolute Boiling point and Absolute Melting point, together with these values for various compounds.

Compound	T_m	a^2 at T_m	$\frac{a_m^2.M}{T_m}$	T_b	a^2 at T_b	$\frac{a_b^2.M}{T_b}$
Sulphur monochloride	197°	6.3*	4.20	411°	3.77	1.23
Phosphorus trichloride	183	4.55	3.41	349	3.02	1.17
Phosphorus tribromide	233	3.16	3.66	443	3.57	2.18
Arsenic trichloride	260	4.19	2.93	403.5	3.10	1.36
Arsenic tribromide	304	3.13	3.22	494	2.30	1.45
Antimony trichloride	346.2	3.79	2.46	496	2.94	1.29
Bismuth trichloride	506	3.78	2.35	—	—	—
Bismuth tribromide	490	2.96	2.70	726	2.28	1.40
Stannous chloride	523	3.04	1.10	876	4.9*	1.1*
Lithium fluoride	1117	28.40	0.06	—	—	—
Lithium chloride	887	18.80	0.89	—	—	—
Lithium sulphate	1122	22.70	2.22	—	—	—
Lithium nitrate	527	13.50	1.75	—	—	—
Sodium fluoride	1253	21.14	0.70	—	—	—
Sodium chloride	1074	14.90	0.81	—	—	—
Sodium bromide	1034	9.29	0.92	—	—	—
Sodium iodide	936	6.51	1.08	—	—	—
Sodium sulphate	1157	19.40	2.39	—	—	—
Sodium molybdate	930	15.6	3.34	—	—	—
Sodium tungstate	967	10.66	3.20	—	—	—
Sodium nitrate	581	12.80	1.86	—	—	—
Sodium metaphosphate	892	18.80	1.46	—	—	—
Potassium fluoride	1129	15.20	0.78	—	—	—
Potassium chloride	1041	13.00	0.93	—	—	—
Potassium bromide	1006	8.54	1.01	—	—	—
Potassium iodide	954	6.49	1.13	—	—	—
Potassium sulphate	1340	15.50	2.01	—	—	—
Potassium bichromate	669	13.00	5.71	—	—	—
Potassium molybdate	1192	13.00	2.60	—	—	—
Potassium tungstate	1194	10.30	2.81	—	—	—
Potassium nitrate	612	12.40	2.05	—	—	—
Potassium metaphosphate	1083	20.70	2.25	—	—	—
Rubidium fluoride	1033	9.24	1.02	—	—	—
Rubidium chloride	999	9.46	1.13	—	—	—
Rubidium bromide	956	6.86	1.19	—	—	—
Rubidium iodide	915	5.83	1.34	—	—	—
Rubidium sulphate	1347	10.73	2.04	—	—	—
Rubidium nitrate	579	8.91	2.24	—	—	—
Cesium fluoride	953	6.03	0.96	—	—	—
Cesium chloride	919	6.60	1.20	—	—	—
Cesium bromide	909	5.42	1.27	—	—	—
Cesium iodide	894	4.80	1.39	—	—	—
Cesium sulphate	1292	7.59	2.13	—	—	—
Cesium nitrate	687	6.78	1.92	—	—	—
Thallium nitrate	479	4.89	2.69	—	—	—

*approximate

Lorenz and Herz start with the hypothesis—which I consider quite unpermissible—that the temperatures of rapid volatilization of some of the salts, *e.g.* LiF, LiCl, NaCl, NaBr, KF, KCl, RbI, CsCl, CsBr, Cs_2SO_4, are very close to their true boiling points, T_b, at atmospheric pressure. Since the approximate temperatures show an almost constant ratio to the corresponding melting points T_m (absolute scale), as determined directly by myself, they first compute the "true" absolute boiling points of

TABLE XXII

Observed and Computed Absolute Boiling points Compared

Salt:	Absolute boiling points	
	Measured at 1 atm.	Calculated by Lorenz and Herz
LiCl	1610°	1304°
NaCl	1698	1579
NaBr	1668	1519
NaI	1563	1376
KCl	1668	1531
KI	1545	1404
RbBr	1582	1406
RbCl	1606	1469
RbI	1549	1346
CsCl	1517	1351
CsBr	1506	1337
CsI	1542	1900

the salts, then their densities at T_b and T_m with their equally constant ratio, after which they extend these considerations over the whole series of salts investigated. Finally, taking for granted the validity of the law of corresponding states, they even proceed to calculate the absolute critical temperatures, T_k, and the critical densities, d_k, of all these salts. Ruff and Mugdan[1] found, by direct boiling-point determinations of some alkali halogenides, values appreciably higher than those calculated by Lorenz and Herz, as is shown by the boiling points collected in Table XXII.

[1] O. Ruff and S. Mugdan, *Z. anorg. allgem. Chem.*, **117**, 147 (1921).

In spite of this evident disagreement, the authors try to demonstrate that these directly determined values of T_b also bear a constant ratio to T_m, although the latter no longer by any means corresponds to the value 1/0.68 postulated by their own theorem, but is now about 1/0.5.

Notwithstanding the remarkable numerical relations that these authors thus find, I am not yet convinced that the rule of corresponding states—which does not hold rigidly even for most other liquids—may be considered valid for molten salts. Until this is better established, all conclusions regarding a possible association of these remarkable liquids lack their very foundation. The next chapter will discuss the possible bearing of the electrical conductivity of molten salts on this problem.

CHAPTER XVII

The Measurement of the Electrical Conductivity of Molten Salts

An exact knowledge of the temperature coëfficient of the electrical conductivity of liquids is of no less importance than is the knowledge of the temperature coëfficient of their molecular surface tension, for those who wish to obtain an insight into the internal molecular state of liquids. A number of investigators have measured the electrical resistance of molten salts having relatively low melting points;[1] but as soon as the temperature of the melting point exceeds about 700° the various results do not agree very well for the same salt, because of the many sources of error in the methods used. The obstacles to accurate measurement increase tremendously above 700°, in particular because the electrical conductivity of most of the insulators used in the apparatus at lower temperatures, gradually increases as the temperature surpasses certain limits, thus making perfect insulation an impossibility.[2] Furthermore, at very high temperatures the reactivity of most compounds with the materials composing vessels and electrodes increases at a steadily increasing rate, so that the electrolytes under investigation become more and more polluted by the resulting reaction products; and since the electrical conductivity of liquids is very strongly influenced by even small traces of impurities, the results must soon become quite unreliable.[3]

[1] K. Arndt, *Z. Elektrochem.*, **12**, 337 (1906); **13**, 509 (1907); **14**, 662, 665 (1908); R. Lorenz and H. T. Kalmus, *Z. physik. Chem.*, **59**, 17 (1907); R. Lorenz and A. Hochberg, *Z. anorg. Chem.*, **94**, 288, 305 (1916); *Z. physik. Chem.*, **79**, 63 (1912); A. Bogorodsky, *J. Russ. Phys. Chem. Soc.*, **40**, 192 (1908); H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, **25**, 469 (1907); A. W. Aten, *Z. physik. Chem.*, **66**, 641 (1909); **68**, 578, 624 (1910); **78**, 1 (1911); R. Lorenz, *Die Elektrolyse geschmolzener Salze* (Halle, 1905).

[2] Roberts Austen, *Engineering*, **59**, 742 (1895); E. Warburg and A. Tegetmeyer, *Ann. Physik*, **21**, 622 (1884); **32**, 442 (1887); **35**, 455 (1888); **41**, 18 (1890); R. Ambronn, *Ann. Physik*, **58**, 139 (1919); F. M. Jaeger, *Anleitung*, p. 132.

[3] F. M. Jaeger, *Proc. Acad. Sci. Amsterdam*, **17**, 329 (1914); Jaeger and Kahn, *ibidem*, **19**, 381, 397 (1916); F. M. Jaeger, *Z. anorg. Chem.*, **101**, 1ff (1917).

Because of the circumstances mentioned, in order to extend the determination of electrical conductivity of molten salts even up to only 1650°, it was first necessary to develop a trustworthy method of measurement. Such a method that has proved itself well suited for the purpose, and apparently giving results as accurate at the highest temperatures attained as at the lower ones, has been worked out by the writer and his collaborators.[1]

The principal difficulties to be overcome may be summarized as follows:

1. The non-checkable deformation of all containers, vessels, supports, electrodes, and other parts, as a consequence of the thermal expansion of the materials used for them.

2. The pollution of the liquids under investigation, due to impurities extracted from the walls of the container and from the electrodes as the result of the chemical interaction between the materials used for them and the molten salts being studied at such very high temperatures.

3. The non-determinable transition resistances occurring at the contacts of electrolyte and electrodes.

4. The irregular and variable temperature distribution throughout the whole extent of any voluminous and unsymmetrically designed apparatus, and the impossibility of avoiding uncontrollable temperature gradients therein.

Among these different factors that cause possible errors perhaps the most troublesome one is the last one because, as we have already pointed out, the space within the furnace that does not show a perceptible temperature gradient and therefore is to be regarded as possessing the properties of a real thermostat is very limited, so that it is a prime necessity to reduce the dimensions of the resistance vessel to the smallest possible ones. This in its turn, however, implies a very delicate measurement of the resistance in relatively thin layers of the liquid.

On the other hand it is necessary to secure a very rapid establishment of temperature equilibrium between the apparatus and its immediate surroundings. Therefore the

[1] F. M. Jaeger and B. Kapma, *Z. anorg. Chem.*, 113, 27 (1920); F. M. Jaeger, *Rec. gen. sci.*, (1919); *Bull. soc. chim. Belg.*, 35, 221 (1926).

apparatus must be constructed of good heat conductors, and must be given as symmetrical a shape as possible in order to guarantee the greatest attainable homogeneity in the temperature distribution surrounding it. Since good heat conductors are also good electrical conductors, these

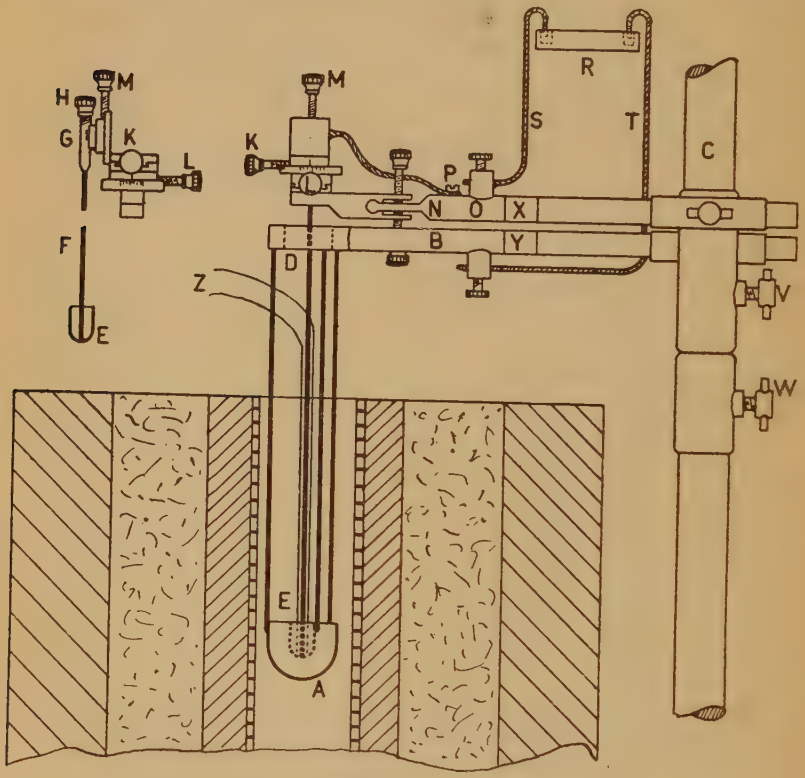


FIG. 105

conditions could be satisfied only by using one of the electrodes itself as the resistance vessel, choosing for the material iridium-free platinum. Since the resistance of these platinum parts can be made as small as possible by suitably selecting their dimensions, and its dependence on temperature can be determined very exactly, the corrections necessary to apply to the results can be made very small and very reliable.

After paying due attention to all these considerations, we have devised the apparatus shown in its final form in Figure 105.

The resistance vessel is appropriately shaped as a hollow hemisphere *A*, of a diameter of 35 mm. and provided with a cylindrical prolongation of 10 mm., the whole being made from a single piece of the purest, iridium-free platinum about 0.4 mm. in thickness. It is permanently attached to a heavy red copper ring *D* by means of three strong iridium-free platinum wires soldered to *A* in the hydrogen-oxygen blowpipe. The wires have a length of 160 mm. The platinum vessel with the wires, the copper ring *D*, and its support *B*, form one electrode; the other electrode *E* has exactly the same form as *A* but its spherical portion has a diameter of only 10 mm. This inner electrode *E* is permanently fastened at *G* and *H* to an adjusting device *MKL* by means of an analogous platinum wire *F* having the same length as the others and a diameter of 1.5 mm. also. The dimensions and the analogous shape of this inner electrode and the vessel *A*, make it possible to center it within *A* in such a manner that *A* and *E* are equidistant and their limiting surfaces accurately parallel with each other.

The inner and outer electrodes are adjusted by means of a device consisting of three slides movable independently of one another and adjustable within the limits set by the three screws *K*, *L* and *M*, almost in the same way as is done in the ordinary crystallographic goniometers. Screws *K* and *L* permit movements from side to side; the screw *M* regulates movements up and down. At any moment the particular position of the slide, and therefore of the inner electrode also, can be read off from a lateral divided scale. The inner electrode can be brought into an exactly vertical position or some other slightly differing from the latter, by means of the device shown at *N* and the accompanying steel spring. This adjustment is secured by means of the vertical screw that runs through it. The platinum wire *F* is held in a slightly conical elastic copper tube with four longitudinal slots; the wire *F* is pinched

firmly into the copper tube by the screw-cap *H* thereby securing an excellent electrical contact also.

The whole slider system is connected with *P* directly by means of a thick copper ribbon, thus eliminating the troublesome transition resistances.

The supports *B* and *O*, as well as the strong wires *S* and *T* are all made from thick copper bars, and connected at *R* to the mercury basins there. The supports *B* and *O* are insulated very satisfactorily by pieces of ivory inserted at *X* and *Y*. The whole device is mounted on a heavy stand *C* by means of strong copper tubes permitting an up-and-down movement that is arrested by means of the set

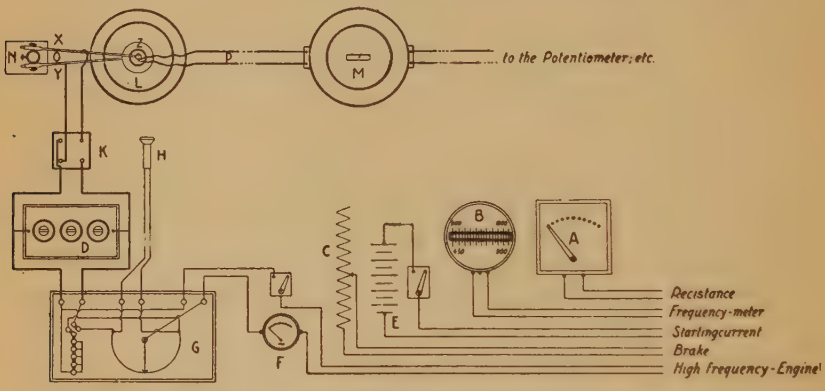


FIG. 106

screws *V* and *W*. The platinum-rhodium wires of the thermocouple are indicated by *Z*. Parallel with the resistance vessel *AE* we use a precision condenser of four decades as a shunt, this being necessary in order to improve the acoustical minimum of the telephone, which is used as a zero-instrument during the measurement of the electrical resistance by means of an alternating current and a precision Wheatstone bridge or analogous instrument.

Method of Measurement. To avoid polarization phenomena the resistance of the cell *AE* must be measured by means of an alternating current. At the very beginning of the experiment, however, there were difficulties due to the unfavorable ratio between the surfaces of the two electrodes. If we are to assume the resistance of an electrolyte

amounting to, let us say, N ohms, then according to Kohlrausch's experience, the heavily platinized electrodes used to obtain a good acoustical minimum in the telephone must have a surface of at least 10/N sq. cm. Evidently it is impossible to satisfy this condition by means of a cell of 40 mm. diameter and having the form described. This fact manifested itself during attempts to calibrate the cell with a potassium chloride solution at ordinary temperatures, even though the electrodes had previously been heavily platinized by Lummer's and Kurlbaum's method. However, if a second cell of the same shape was inserted into the second branch of the Wheatstone bridge, so that the arrangement was now a symmetrical one, a good telephone minimum appeared to be obtainable. At furnace temperatures this method must be considered impracticable, so that another one had to be sought. We finally hit upon the device of replacing the usual inductorium by an adjustable Siemens-Halske high-frequency oscillator which produces a homogeneous, purely sinusoidal induction wave, which is not obtained from the common inductorium.[1] At the same time an adjustable electrostatic condenser was inserted in the circuit in parallel with the cell so that its electrostatic capacity could be varied, if necessary, within certain limits. The frequency of the oscillator could be regulated between 450 and 1800 interruptions per second by means of a brake, and checked by means of a frequency-meter.

The apparatus makes much noise; it must therefore be installed in a distant room and wrapped in carpets. The rheostats, oil capacity-brake, frequency-meter, and the rest, however, were arranged in the immediate neighborhood of the measuring apparatus (see Figure 106) which consisted of a cylindrical Kohlrausch bridge of Leeds-Northrup construction. In Figure 106, *G* is the revolving Kohlrausch bridge; *F* is an amperemeter indicating the intensity of the alternating current; *D* is the electrostatic decade-capacity parallel with the cell; *B* is the frequency-meter; *E* is the storage battery providing the current to

[1] E. W. Washburn and H. E. Bell, *J. Am. Chem. Soc.*, 35, 177, 1430 (1913); W. A. Taylor and S. F. Acree, *ibidem*, 38, 2396, 2403, 2431 (1916). A Vreeland oscillator made by the Leeds-Northrup Company can also be successfully used for this purpose.

regulate the magnetic field of force; *C* is a rheostat for controlling the number of revolutions of the oscillator, whose motor is started by means of the resistance *A*; *H* is the telephone; *KLOP* is the complex of apparatus described and represented in Figure 105; *M* is the ice-box. The potentiometer complex is omitted in Figure 106.

A non-induction Wheatstone bridge with decades (O. Wolf, Berlin) was tried at first; but in this case seemed to be less suited to our purpose than the revolving cylindrical screw-bridge of Kohlrausch.

However, the Leeds-Northrup apparatus could not be used in precisely the form as sold on the market. It was necessary to check all its connections carefully, to grind the conical plug openings until there was no longer any variation in the resistances of these connections when the plugs are thrust into their holes more or less tightly, and also to calibrate the divided scale in order to check the 500 cm.-long manganin wire wound spirally in the grooves of the porcelain drum. Having once established a correction-curve for the instrument, it is possible to read, by means of the vernier and alidade of the drum, as close as 0.0001 portion of the wire length, *i.e.* to about 0.5 mm. in the 5 meters of its length.

Contrary to what has been recorded in the literature, we found that the platinizing of the electrodes is of undeniable advantage for work at very high temperatures also. It is true, the black surface does not survive at these temperatures, but the platinum particles will stick to the electrode surface as very small droplets, just as if they had been soldered to it with the hydrogen-oxygen flame, so that the surface of the electrode becomes quite rough as if treated with a sand blast. Experience taught us that this condition of the electrode—especially of the inner one—is very favorable for obtaining a well-defined acoustic minimum in the telephone.

As regards the temperature measurements, reference may be made to what was said about them when considering measurements of the surface tension. The accurately centered thermocouple was connected directly to the inner electrode, the wires being insulated by Marquardt-porce-

lain capillary tubes. The hot junction was placed within the spherical cavity of the inner electrode, the cold junction being connected with the icebox.

It appeared to be strictly necessary to keep the lower end of the furnace closed during the course of the measurements. In this way the furnace temperature can be kept so constant that even at 1600° it does not change more than 0.2 degree within a period of 12 minutes—provided that before each measurement it is kept at a given temperature for a not too short interval of time.

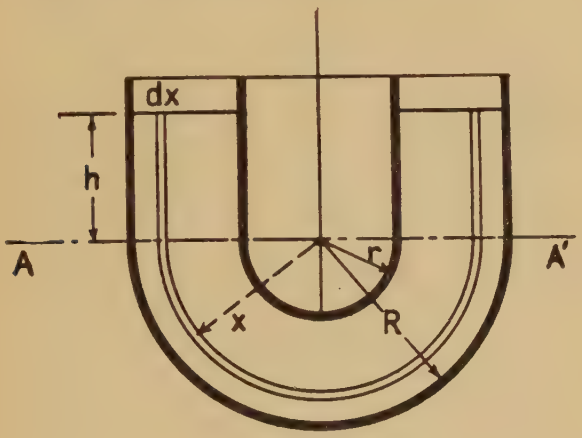


FIG. 107

After these preliminaries have been gone through, the first step is to determine the resistance capacity C of the cell, and its variations due to inadequate adjustment of the inner electrode.

Calling the specific conductivity of the electrolyte in ohms^{-1}, κ, and the resistance capacity of the cell C, then the measured resistance, W, of the liquid in a prismatic cell having a length l and a cross section d is given by the equation

$$W = \frac{l}{\sigma} \cdot \frac{1}{\kappa} = \frac{C}{\kappa}$$

In the case of the platinum vessel used by us the value of C can be calculated directly from its dimensions, provided that the equipotential surfaces in the liquid are

parallel with the walls of the vessel when the electric current passes through the electrolyte. Experience shows that such is very nearly the actual case.

If the radius of the outer vessel is R, and the radius of the inner spherical space is r, and if the liquid rises in the cell to a height h above the medial plane AA' of the concentric spheres (Figure 107), then an infinitely thin layer of the liquid will have the volume $\frac{dx}{2\pi x^2 + 2\pi xh}$. The volume of the whole vessel filled with liquid will then be

$$\frac{1}{2\pi}\int_r^R \frac{dx}{x^2 + hx} = \frac{1}{0.8686\pi h} \cdot \log_{10}\frac{R(r+h)}{r(R+h)}$$

This formula holds in our case, as was shown by comparing the calculated and the observed values of C. For example, in one experiment C = 0.1595 and the computed value was 0.1577. Usually, however, the capacity was determined experimentally, solutions of potassium chloride of known concentrations being used as standard liquids. Since the coëfficient of expansion of platinum is accurately known, the change of C with increasing temperature is readily calculated. As a check, experimental determinations at different temperatures subsequently were made with molten potassium nitrate, after measuring accurately its specific conductivity at different temperatures.

To determine the thermal expansion of the platinum vessel we used the formula:

$$l_t = l_0(1 + 8.8868 \times 10^{-6}t + 1.324 \times 10^{-9}t^2).$$

For the variation in density of the molten salts with temperature we used the formulas determined by ourselves and by Goodwin and Mailey.[1] The following will serve as an example of the determination of C: at 364.1° the vessel-resistance, when filled with 27.80 gm. of KNO_3, was 0.3001 ohms. We had previously determined that at this temperature the specific gravity of the salt = 1.849, and its volume = 15.03 cu. cm. From the C,V-curve of the apparatus at 20°, C (at 20°) = 0.1790. The dimensions of the vessel at 20°, R = 1.820 and r = 0.488 cm., and the dilata-

[1] Jaeger and Kahn, *Proc. Acad. Sci. Amsterdam*, 19, 381 (1916); H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, 25, 469 (1907); 26, 28 (1908); R. Lorenz, H. Frey and A. Jabs, *Z. physik. Chem.*, 61, 471 (1909).

tion formula of platinum give us the values of the dimensions at 364.1° and show that at this temperature the capacity = 0.1815.

Since the resistance of the connection to the cell at 364.1° = 0.0449 ohms, the resistance of the salt is 0.2552 ohms; therefore at 364.1° the specific conductivity κ = 0.1815/0.2552 = 0.711 ohm.

Another circumstance which must be taken account of in considering the resistance capacity, C, is the influence that an inadequate adjustment (Fig. 105) of the inner electrode *E*

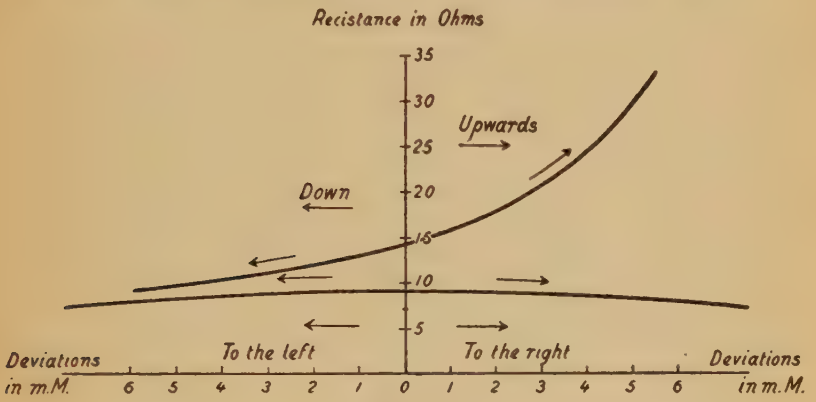


FIG. 108

with reference to the outer electrode *A*, must have on the value of C. We studied this influence using 1/10*N* solutions of potassium chloride, both electrodes being coated with platinum-black. Starting with the inner electrode in the central position, it was shifted to the right, to the left, up, down, and so on through accurately measured distances and the cell resistance was determined for each case. The results of this study are presented graphically in Figure 108. It is apparent that shifting to the left or to the right of the central position, but along a horizontal plane, exerts much less influence on the cell capacity than a shift of the inner electrode upward or downward. Therefore one must exercise much greater care that the inner electrode is adjusted in the proper horizontal plane, than in placing it in an accurately co-axial position.

When the inner electrode is horizontally eccentric, the cell resistance evidently diminishes more rapidly as the eccentricity increases—to be expected *a priori*. The horizontal eccentricity is the less important, however, since a shift of 1 mm. of the electrode from its central position diminishes the cell resistance by only 0.3 per cent of its value. Since co-axial adjustment can be made with an accuracy of at least 0.1 mm., it is not necessary to make special arrangements for eliminating these insignificant errors.

The greater errors arise from the vertical eccentricity: a shift of 1 mm. vertically can change the value of the cell's capacity by 10 per cent. But the correct central adjustment of the inner electrode can be made with high precision and without the aid of special devices. If both electrodes are accurately shaped, it is sufficient to take care that the upper edges of the cylindrical portions of the two electrodes are brought into precisely the same horizontal plane. The adjustment device already described and a laterally placed telescope make this easily possible. We found that the adjustment could be reproduced within 0.03 per cent of the correct value; while in the worst cases both sources of error combined cause a maximum uncertainty of 0.06 per cent of the cell's capacity.

The greatest care must be taken to avoid any deformation of the cell or of the electrodes, not only during the measurements but afterward when the molten salts have cooled sufficiently to begin to solidify. It was found necessary to empty out the molten salts immediately after the measurements were completed and while the melt was still liquid.

Measurements were made as follows. First, the resistance capacity of the cell is determined for the standard liquid at different heights h in the cylindrical part of the cell. Then the pure, finely powdered salt is placed in *A* (Figure 105) in such quantity that, after it has melted, both electrodes will be adequately immersed in the liquid. If we know exactly the weight of the salt used and its density in the solid and in the liquid states at several temperatures, then we have all the data necessary for deter-

mining h. Next, the electrodes are carefully centered, and after the salt has been melted their mutual positions are checked once more—which is accomplished by shifting the whole apparatus upwards by means of the sliding tubes of the support *C* and the clamps *V* and *W*. If everything is all right, the vessel *A* is lowered into the furnace until it is within the region of uniform temperature, and the furnace is then maintained uniformly and for a long time at the constant temperature at which the measurements are to be made. The resistance is now determined, and re-

TABLE XXIII

Sodium tungstate: Na_2WO_4

Temperature °C	Resistance (ohms)	Specific gravity d_4	Volume of the salt (cu.cm.)	Capacity	Specific Conductivity κ ($ohms^{-1}$)	Molecular Conductivity φ ($ohms^{-1}$)
752.5	0.1706	3.843	14.315	0.1862	1.091	83.50
800	0.1574	3.799	14.505	0.1846	1.192	92.25
958	0.1194	3.648	15.108	0.1814	1.519	122.50
996.6	0.1065	3.613	15.255	0.1765	1.598	130.05
1066	0.0996	3.554	15.508	0.1713	1.718	142.15
1161	0.0880	3.479	15.534	0.1667	1.893	160.00
1209	0.0804	3.443	16.016	0.1631	1.990	170.05
1260	0.0778	3.406	16.188	0.1622	2.083	179.80
1361.5	0.0702	3.339	16.517	0.1581	2.250	198.21
1412	0.0650	3.308	16.676	0.1549	2.335	207.59
1501	0.0628	3.258	16.939	0.1518	2.453	221.35

Weight of the salt used: 55.10 gm.

The specific weight at each temperature is calculated from:

$$d^t_4{}^\circ = 3.673 - 0.0009275(t - 930) + 0.000000337(t - 930)^2.$$

The value of φ can be very well represented by the equation:

$$\varphi = 83.50 + 0.185(t - 750).$$

determined after a few minutes interval. The temperature of the furnace is then raised, kept constant for a certain length of time and a new series of measurements is begun.

When the properties of the salts are not unfavorable, it has been found that the measurements can be reproduced within 0.1 per cent of the same values, even at the highest temperatures. In this respect the method is adapted to yielding all that one may require of it.

Of course eventually the special properties of the salts employed may present serious difficulties, particularly at the higher temperatures, just as was the case in measuring

the surface tension. The extreme volatility of some salts at higher temperatures is particularly likely to create a serious obstacle. Another unfavorable circumstance arises from the fact that at high temperatures, in part because of incipient dissociation and in part because of the interaction of atmospheric water vapor and carbon dioxide, some alkali salts give an evident alkaline reaction; moreover,

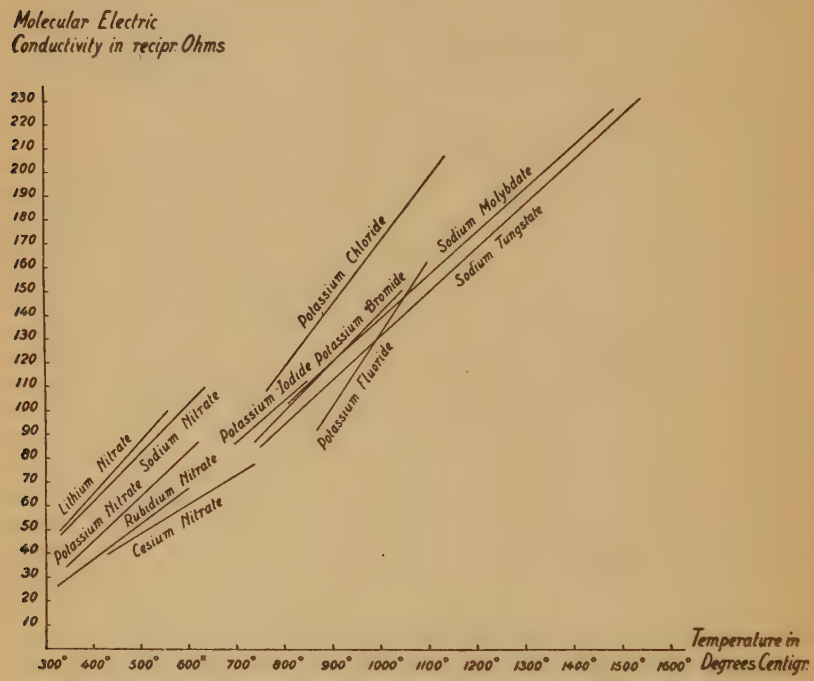


FIG. 109

above 500° the nitrates show an evolution of oxygen. Such a series of measurements is illustrated by the results obtained for sodium tungstate given in Table XXIII.

The following salts were studied by the above method: $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$; KF, KCl, KBr and KI; Na_2MoO_4 and Na_2WO_4. The values obtained for the molecular conductivity are represented graphically in Figure 109; and the corresponding specific conductivities, κ, are given in Figure 110.

These data seem to justify the following general conclusions:

1. Both the specific and the molecular electrical conductivities of all these molten salts are linear functions of the temperature. The only exceptions are the κ,t-curves of Na_2MoO_4 and Na_2WO_4, which are slightly concave toward the temperature axis.

2. The mutual positions of the specific conductivity curves for the alkali nitrates and halogenides, show in a

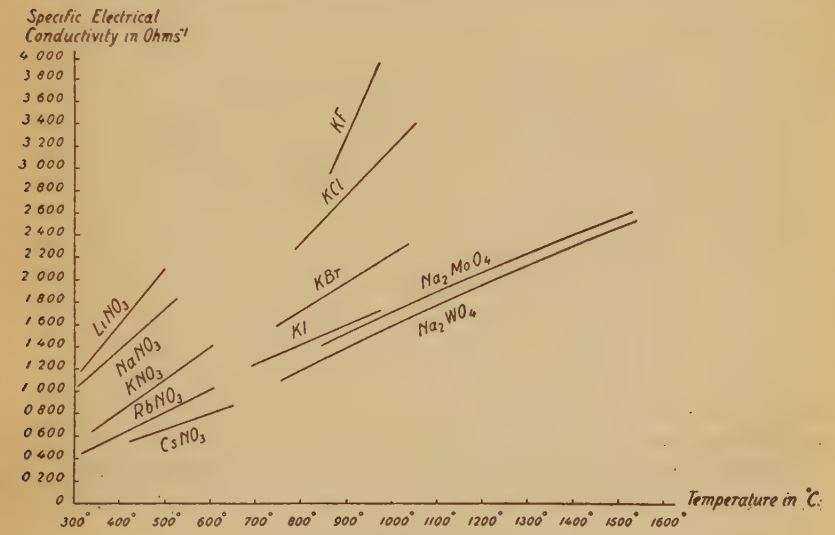


FIG. 110

general way the same regularity that they have shown in previous cases. Here also the lower curves correspond to the greater atomic weights of the alkali metals (see nitrates) or of the halogen atoms (see potassium halogenides). Furthermore, the curve for sodium tungstate lies below that for sodium molybdate.

A new feature, compared with the χ,t-curves, is present here, however, in so far as the temperature coëfficients of the specific electrical conductivity are larger, the smaller the atomic weight of the alkali metal (nitrates), or of the halogen atoms (potassium salts). For example, the κ,t-curves for KCl, KBr and KI intersect each other at almost

exactly 430°; however, the fluoride occupies an eccentric position with reference to the alkali halogenides.

It is a remarkable fact that, except in the case of the alkali nitrates, these regularities are not met with when we consider the molecular conductivities instead of the specific ones. A similar situation was found when considering the specific and the molecular surface energy of these salts. These "molecular" properties seem not to have the same significance as the specific properties for the molten salts.

The question as to whether the electrolytic dissociation of these salts is partial,[1] or total,[2] cannot be decided at this time. In general it would seem that the state of dissociation of these liquids does not vary appreciably with temperature,[3] but that the increase in electrical conductivity with increasing temperature is largely dependent upon the decreasing internal friction; in all of them viscosity decreases with rising temperature. Regarding the efforts to prove that the degree of dissociation, α, undergoes a variation when they are dissolved in other salts having an ion in common with them,[4] it must be stated that Bray[5] has brought forward very telling arguments against this view. It seems to be generally agreed, however, that there is a feeble variation in their state of dissociation with a change in temperature. Many authors have emphasized also the remarkable linear relationship between the temperature and many properties of such molten salts. This fact seems to indicate that in all cases the molecular condition of these liquids must be a comparatively simple one.

[1] R. Lorenz, *Die Electrolyse geschmolzener Salze*, loc. cit.
[2] K. Arndt, *Ber.*, 40, 2937, 3612 (1907).
[3] H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, 25, 469 (1907); 26, 28 (1908).
[4] O. Sackur, *Z. physik. Chem.*, 78, 550, 564 (1912); 83, 297 (1913).
[5] W. C. Bray, *Z. physik. Chem.*, 80, 251, 378 (1912).

CHAPTER XVIII

The Measurement of the Internal Friction of Molten Salts

In previous chapters we have drawn attention to the fact that the viscosity of liquids, and its dependence on temperature, is an important factor in many phenomena; furthermore, it is also of the greatest importance that we should understand it thoroughly because of its possible influence on determinations of surface energy, density, and electrical conductivity of molten salts.

These considerations have stimulated us to develop, in my laboratory, a reliable method for the exact determination of the internal friction of molten salts and its relation to temperature. The present chapter will discuss in a more particular manner the successful work carried out under my supervision by my pupil, Dr. R. S. Dantuma.[1] Most methods for determining viscosity at higher temperatures seem to be unsuited for securing reliable results, not for theoretical reasons but because of the large number of sources of error that are introduced whenever previous forms of apparatus are used at high temperatures. It requires accurate study of all the subordinate details of the experimental arrangements hitherto used under such extreme temperature conditions, and a careful comparison of the advantages and the disadvantages of each method, in order to make a suitable choice among them.

Before taking up the subject in detail, we may profitably review in brief some of the fundamental ideas involved in the theory of internal friction, the coëfficient used to measure it, and the units in which it is expressed. We must also consider briefly previous methods of demonstration and the reasons for rejecting them.

[1] R. S. Dantuma, Thesis (Groningen, 1927); *Z. anorg. allgem. Chem.*, **175**, 1ff (1928).

Suppose that a liquid *L* (Figure 111) is of such a nature that it "wets" the plane fixed wall *AB* of the container. Suppose also that *L* is flowing past and parallel with *AB* at a velocity equal to v at the point *P* located at the distance s from the wall. Now if v is not sufficient to produce turbulency in the liquid *L*, the motion actually taking place in the liquid may be described as follows. The thin layer of liquid in immediate contact with *AB* adheres to the wall so tenaciously that it does not acquire any motion with respect to the wall. The more distant portions of the liquid move as though the latter consisted of an infinite number of infinitely thin films which, between the wall and the point *P*, are all moving past each other, and parallel with the wall, at velocities that gradually increase in such a manner that each film attains a velocity proportional to

FIG. 111

the distance of the film from the wall, dv/ds remaining constant and the velocities ranging between zero and v. The gradual decrease in velocity of the successive films, from that at *P* to the stationary one adhering to *AB*, is related to an apparent resistance due to the interchange and loss of kinetic energy of molecular motion in each of these films transmitted from their contact surfaces. The total friction per unit surface experienced by the liquid at the wall *AB* is therefore identical with the sum of the internal frictions of all the subsequent infinitely thin layers moving past each other. This internal friction of the liquid is measured by the amount of work required to move two parallel liquid layers 1 cm. apart, and each having an area of 1 sq. cm., at a relative velocity of 1 cm. per sec. This amount of energy is called the coëfficient of internal friction, η, whose dimensions in the absolute

system are g.cm.$^{-1}$ sec.$^{-1}$. The "viscosity" of the liquid is determined by this coëfficient of internal friction, η.[1]

There are two principal kinds of methods for measuring η: either the wall AB is fixed and the liquid flows past it, or the wall is moved through the liquid. In both cases the velocity of motion must be so regulated that no turbulency is set up in the liquid.

The first method is that made use of in all viscosimeters. These measure the time required for a definite volume V of liquid to flow, under a known pressure-difference, through a capillary tube of precisely determined dimensions. If there is no turbulency, so that each flowing particle moves parallel with the axis of the tube at a velocity proportional to its distance from the tube wall, the coëfficient η is given by Poiseuille's formula:[2]

$$V = \frac{\pi p r^4}{8 l \eta} T$$

where r is the radius of the capillary, l is its length, p is the pressure-difference, T the time required, and V the volume of liquid passing through the tube in the time T. This formula was subsequently corrected by Hagenbach.[3]

Although some investigators[4] have occasionally used this method in studying molten salts, its employment at higher temperatures presents the same difficulties that were encountered in measuring the surface tension of molten salts by means of the capillary rise of the liquid in a glass tube. Not only are the walls of the tube corroded by the molten salts, and the more rapidly the higher the temperature; but it also seems to be impossible to keep the temperature constant throughout the whole extent of the

[1] The coëfficient of internal friction, η, is also defined as the force exerted on each other by two liquid layers, having an area of 1 sq. cm., situated in a current whose change of velocity measured perpendicular to the two layers ($= \partial v/\partial s$) is equal to 1. It follows from this that the magnitude of η is $MLT^{-2}/L^2T^{-1} = ML^{-1}T^{-1}$ = g.cm.$^{-1}$ sec.$^{-1}$. In a liquid under a constant hydrostatic pressure, p, and flowing through a tube of radius r, the distribution of the current velocities over a cross-section of the tube is represented by a paraboloid of revolution having its major axis coïncident with the tube axis. For the details of these phenomena see the literature on the subject.

[2] Poiseuille, *Compt. rend.*, **15**, 1167 (1842); *Ann. Physik*, **58**, 424 (1845).

[3] E. Hagenbach, *Ann. Physik*, **109**, 385, 402 (1860). For other corrections and changes in Poiseuille's formula *see* O. Reynolds, *Trans. Roy. Soc. London*, **174A**, 935 (1888); M. Reiner, *Kolloid-Z.*, **39**, 80 (1926) and elsewhere.

[4] R. Lorenz and H. T. Kalmus, *Z. physik. Chem.*, **59**, 244 (1907).

mass of the apparatus. Moreover, in this form the method can be used over only a very limited temperature range. These considerations led us to reject this method for our work.

The second kind of method, in which the wall S is moved through the liquid L, was made use of by Coulomb.[1] He observed the gradual diminution in the amplitude of a freely-swinging solid sphere or ellipsoid suspended in the liquid by a thin, twisted wire. The internal friction of the liquid gradually damps its oscillations and the energy thus consumed may be used to determine the coëfficient η. In this case also, the velocity of the moving body must not be too great with reference to the surrounding liquid, otherwise turbulent motion will be set up in the latter. In a modification of this method, a cylinder suspended in the liquid is rotated at a constant angular velocity about its axis. The liquid transfers this motion to a second coaxially suspended cylinder which is thus brought into a constant angular deviation from its equilibrium position as soon as the torsion of its suspension-wire counterbalances the force exerted by the liquid upon the inner cylinder.[2]

Coulomb's method has been employed by several investigators working on molten salts, and has given moderately good results.[3] Its theoretical basis has since been thoroughly studied by Verschaffelt,[4] who with Nicaise has successfully employed it for determining the coëfficient of internal friction of liquefied gases at very low temperatures.

In principle, the method of observation is as follows: A solid of suitable form (sphere, ellipsoid, cylinder) is

[1] C. A. Coulomb, *Mem. Institut*, 3, 246 (1802); A. Le Roux, *Compt. rend.*, 180, 914 (1925); G. G. Stokes, *Trans. Cambridge Phil. Soc.*, 9, 8 (1851); etc.

Stokes measures the velocity of a spherical solid falling vertically through a very viscous liquid. This method is practicable with very viscous liquids only. The method by determining the weight of droplets falling from a capillary of known radius, is not suited for obtaining reliable and accurate results, and cannot be brought into a form suitable for work at very high temperatures. Measurements of molten salts by this method have been made by C. Dölter, *Sitzb. Akad. Wiss. Wien, Abt. I*, 114, 529 (1905), and by K. Arndt, *Elektrochem. Z.*, 13, 578 (1907).

[2] Le Roux, *loc. cit.*

[3] C. F. Fawsitt, *Proc. Roy. Soc. London*, 80A, 290 (1908); E. W. Washburn, *Rec. trav. chim.*, 42, 686 (1923); R. Lorenz and A. Höchberg, *Z. anorg. allgem. Chem.*, 94, 317 (1916).

[4] J. E. Verschaffelt and C. Nicaise, *Comm. Phys. Lab. Univ. Leiden*, No. 148-b-c-d (1915); No. 149-b (1916); No. 151 (1917); No. 153 (1919).

suspended at the end of an elastic wire. Moderate torsion of the wire causes the body to perform harmonic oscillations and, if the deviations from the position of equilibrium are small, the torsional force in the wire will be proportional to the instantaneous deviation. If now the oscillation of the body is damped by any force which, at each moment, is proportional to the velocity of the motion, then the damped oscillations preserve their harmonic character. The subsequent amplitudes decrease, each being smaller than its predecessor by a constant fraction $1/k$ of the latter. If A_p is the amplitude after p oscillations, and if k is greater than 1:

$$\frac{A_p}{A_p+1} = \frac{A_q}{A_q+1} = k$$

The value $\delta = \log_{10} k$ (or ${}^e l_n\, k$) is called the "logarithmic decrement" and since $A_p = k^n A_{p+n}$, we have $\delta = \frac{l_n A_p - l_n A_{p+n}}{n}$, or in general: $\delta = \frac{l_n A_p - l_n A_q}{q-p}$. As long as δ is small, the time of the undamped oscillation, t_0, of the body remains practically unaffected by the damping; in fact, $t = t_0(1 + \delta/\pi^2)^{\frac{1}{2}}$ where t is the time of the damped oscillation; therefore δ must be relatively large before t becomes appreciably different from t_0. This logarithmic decrement δ must be measured before one can calculate the coëfficient η.

Verschaffelt has deduced the necessary relations by assuming that the oscillating body is a sphere of radius R suspended from a wire so very thin that its diameter may be neglected. The vessel containing the liquid must be so wide that its wall exerts no influence upon the liquid, that is that the waves generated in the liquid by the oscillating sphere will be totally damped out before they reach the wall of the vessel; or, if they are reflected by the wall, then they are totally damped before again reaching the oscillated sphere. When these conditions are fulfilled, the coëfficient of internal friction η may be found from the equation:

$$(2+p)\eta + \gamma R\sqrt{nd} = \frac{3L'}{8\pi R^3}$$

in which $p = \frac{bR + 1}{R^2b^2+(bR+1)^2}$; $b = \left(\frac{\pi d}{\eta t}\right)$; $L' = \frac{2\delta K}{t_0}$; $\gamma = (\pi/t)^{\frac{1}{2}}$

In these formulas R is the radius of the oscillating sphere; t = the damped oscillation time in the liquid; t_0 = that in the air; K = moment of inertia of the whole oscillating system; d = specific gravity of the liquid; δ = the true observed logarithmic decrement. K is determined by observing the times of oscillation t_1 and t_2 of the system. After additional weights of known inertia-moments K_1 and K_2 have been combined with the system K is found from the relation: $\frac{t_1}{t_2} = \left(\frac{K + K_1}{K + K_2}\right)^{\frac{1}{2}}$

The actually measured damping δ', is that of the whole oscillating system and is composed of the following factors:

The damping δ exerted by the liquid upon the immersed moving sphere;

The damping exerted by the air upon the portions of the moving system that are outside the liquid;

The internal friction of the suspension wire.

Calculation shows, that the observed logarithmic decrement δ', must be diminished by the decrement δ'' that would be observed if there were present only the first and second damping factors just mentioned.

One may determine this correction by the following method: First, determine the logarithmic decrement δ' of the whole moving system, *i.e.* the sphere plus its additional weight. Second, the additional weight is replaced by another having the same form but made of such material that the difference in weight and momentum of inertia between the two additional weights is exactly equal to the weight and moment of inertia of the sphere used. The sphere is removed before substituting the second weight for the first one. By this means it is assured that the shape of those portions of the system outside the liquid remains exactly the same in both cases, while neither the total weight nor the moment of inertia of the whole system is changed. Next the logarithmic decrement

δ'' is redetermined; and the difference $\delta = \delta' - \delta''$ is the true value corresponding to the friction of the sphere alone in the liquid. This is the value of δ used in the above formula. One may neglect the buoyancy of the sphere in the liquid since this correction, although theoretically necessary, seems to be practically of no importance.

Since this latter method is rather difficult of execution it was modified as follows: First, determine the logarithmic decrement δ' when the sphere is immersed in the liquid. Then determine the value δ'' in air while the system, at exactly the same temperature, is suspended in the air close to but above the liquid. The difference $\delta' - \delta''$ is the decrement of the sphere corresponding to the friction of the liquid, but diminished by the decrement δ''' corresponding to the friction of the sphere in the vapor. This value δ''' could be calculated and was added to the difference just mentioned, so that $\delta = (\delta' - \delta'') + \delta'''$ is the value to be used in the above formulas.

We will now describe the apparatus and the manner of carrying out the experiments.

Since one has continually to regulate the temperature of the furnace and simultaneously observe the oscillations of the sphere in the liquid, it was not well possible to get along without two observers unless some recording method was employed. This led to the introduction of a photographic registration of the oscillations, a method having the additional advantage that all details of the experiment are recorded, so that they may be studied later at leisure and quantitatively evaluated.

The photographic recording device has a small mirror attached to the wire from which the platinum sphere is suspended, and a beam of light after reflection by the mirror fell upon a photographic paper fastened to a horizontal rotating cylindrical drum. A complete oscillation of the point of light from side to side impressed a kind of sinusoidal curve on the 35-cm. long paper. The amplitudes of succeeding deviations gradually decrease and can be measured with great accuracy directly on the paper. A time record could be marked accurately on the same paper

by causing a pendulum to periodically intercept the beam of light, so that the time marks on the developed paper appeared as very short interruptions in the curves (See Fig. 115b). This method permits the observer to devote his whole attention to the temperature control and the supervision of the furnace.

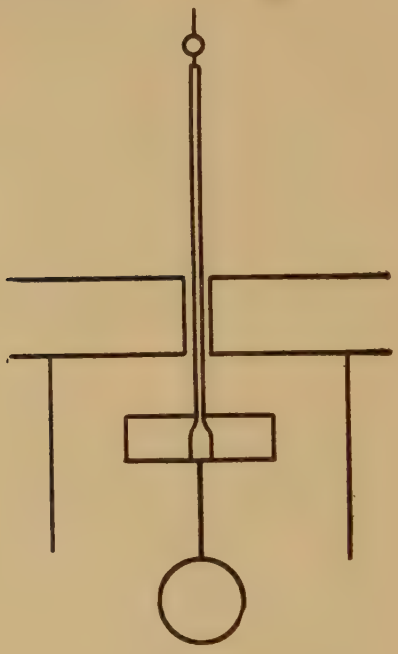


FIG. 112

We used a sphere of pure platinum 2 cm. in diameter centrally attached to a platinum bar 1.5 mm. in diameter and 50 mm. long. Owing to the high specific gravity of the metal (about 22) the sphere's moment of inertia is sufficiently great, in spite of its small volume, to permit the use of an additional weight somewhat smaller than would have been possible otherwise. The bar of platinum was attached to a nickel bar 4 mm. in diameter, and to this bar the centrally perforated additional weights could be attached at a point about 5 cm. above the sphere. Since the center of gravity of the moving system must be kept as low as possible (Figure 112) it is not practicable to add

these weights at the upper end of the bar; furthermore slight errors in the adjustment of the sphere or of the additional weights, and feeble convection currents in the air, appeared sufficient to cause a horizontal vibration of the suspended sphere. The arrangement here figured and adopted has many advantages: a low center of gravity; convection currents occur only within the furnace, since no significantly voluminous parts extend beyond it; the heat conducted through the protruding thin bar of nickel is supplied chiefly from the great mass of the additional

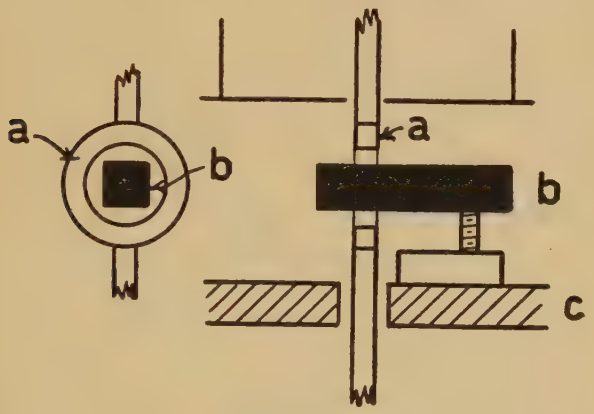


FIG. 113

weights, which is sufficient to prevent a fall in temperature in the immersed sphere on this account. A disadvantage of the adopted method is the absolute necessity of taking all possible precautions to prevent heat radiation to the upper end of the bar where the mirror is attached, and to the suspension wire. Another serious source of error requiring elimination, was due to the influence of the air currents just over the furnace. To eliminate this, the protruding nickel bar first passed through a double-walled water screen (Figure 113, *c*) placed above the furnace. In addition, the nickel bar was interrupted by the ring *a* freely moving about the copper block *b* and surrounded by a cylindrical mantle of zinc. The block *b* and the ring *a* also were surrounded by a cylindrical mantle cooled by contact with the water screen *c*. By means of these devices

any harm arising from convection currents seems to have been completely prevented, even at temperatures of 1000°. In all cases the logarithmic curves obtained were quite undistorted.

Special precautions were taken to insure a central suspension of the wire and to regulate the magnitude of its torsion. The former was secured by clamping the wire between small steel plates adjustable horizontally by means of a finely divided screw. The torsion was controlled by a table moving around the axis of the apparatus through an angle that was accurately determined by means of a tangential screw. Details of the construction will be found in the original description.[1]

Since the furnace temperature must be kept rigorously constant, and temperature distribution within the furnace must be as uniform as possible, a special construction was necessary for the furnace, particularly since the dimensions of the crucible containing the molten salt had to be rather appreciable in this work so that the whole complex within the furnace had to have a considerable volume. Furthermore, we have to deal with a moving system whose metallic parts are swinging within an electrical field and must avoid disturbances arising from the possible generation of Foucault induction currents. This requires that the electric heating current be shut off during the actual making of the measurements; yet notwithstanding this the temperature within the furnace must remain as constant as possible. Such an objective can be realized only if the thermal capacity of the furnace is very large and the furnace itself has perfect temperature insulation.

The device that we constructed to meet these requirements is shown in section in Figure 114 and may be described as follows. The external mantle of the furnace was a galvanized iron vessel, *c*, 36 cm. in diameter and 40 cm. in height, covered on the outside with a thick sheet of asbestos. The inner cylinder *d* and its floor were also made of iron 1 cm. thick, to prevent the electrical fields caused by the heating currents in the coils *B* and *A* from penetrating the interior of *d*. The circular portion *A* con-

[1] R. S. Dantuma, *Z. anorg. allgem. Chem.*, **175**, 17 (1928).

sisted of three alundum tubes *a* upon which the heating coil was wound in such a manner as to produce a double-sided heating element. This element was inclosed by the iron support which shields the interior of *d* from its field.

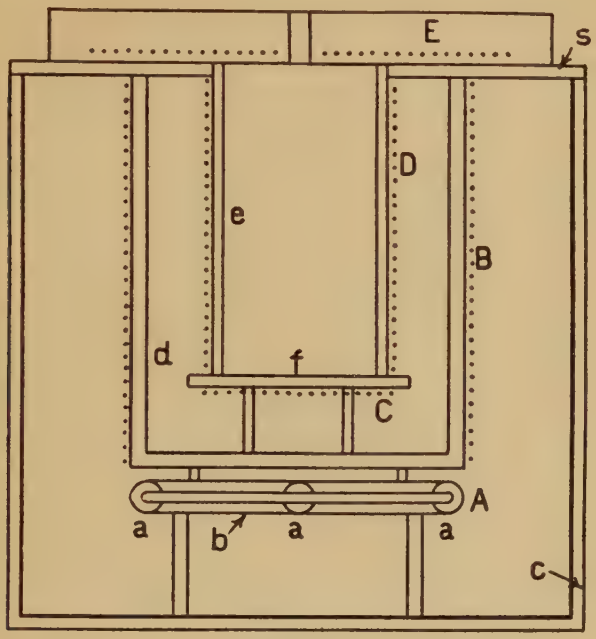


FIG. 114

A porcelain cylinder *e* was placed within *d* and cemented to the perforated porcelain plate *f*. The cylinder *e* and its floor, *f*, were surrounded by the heating-coils *D* and *C* of "Brightray"-nichrome wire 0.8 mm. in diameter and having a resistance of about 2.25 ohms per meter at room temperature. These coils were held in place by a refractory clay, the so-called "Pyruma Putty". The different parts were carefully insulated from one another and supported by alundum tubes. The cover *E* was a disk of refractory clay 5 cm. thick and cut in half diametrically with a central opening. Heating coils of the same kind as those described, were cemented to the underside of each half of the cover. The cover was supported by a layer of asbestos *s*, under which the four lead-wires of the different heating elements

passed outside the furnace. Each heating element was connected in series to a resistance, and joined to a direct-current source of 220 volts; thus the current in each element could be regulated to within 1 to 4 amperes, if necessary.

The spaces between *e* and *d*, and between *d* and the outside galvanized iron mantle, were filled with calcined magnesia. If the furnace were heated so that its temperature in the vicinity of the outside cylinder was 10 or 20 degrees higher than that within the inner chamber, then the current in *D* and *C* could be cut off and the furnace temperature would not fall appreciably during a certain time interval. By keeping the furnace at a constant temperature for 20 or 30 minutes its internal temperature change would not set in before 5 or 10 minutes had elapsed, because the great heat capacity of the furnace and its great mass of insulation made the furnace very slow in cooling. The measurements could be made within about 4 minutes and by previous careful regulation over a long period the furnace temperature then would not drop more than 0.5 degree during each series of measurements. The round-bottomed, cylindrically-shaped platinum crucible containing the molten salt was placed within the inner cylinder *e*. The shape and arrangement of the crucible, 7 cm. high and 5 cm. in diameter, is shown in Figure 115a together with the platinum sphere and the thermocouple. The crucible was supported by an alundum cylinder resting on three insulated supports on the internal furnace-cylinder.

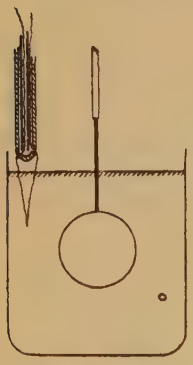


FIG. 115a

All the temperature measurements were made in the usual careful way by means of a calibrated potentiometer (0.01 ampere) and a Moll galvanometer; all parasitic thermoelectric forces were eliminated. A second thermocouple was placed in the insulating material about 1.5 cm. distant from the inner iron cylinder. Of course all connecting wires were insulated with the utmost care by means of paraffine-coated glass plates and the like.

In the recording apparatus the horizontal drum carrying the "Orthobrom" photographic paper had a length of 35 cm. and a diameter of 21 cm. It was turned by a phonograph motor provided with an air regulator that kept its speed constant at 1 cm. per second during a full hour. The whole apparatus was kept in the dark, save for the narrow beam of light reflected by the small mirror and restricted by a vertical slit in front of the same. This beam of light fell upon a cylindrical lens, formed by a tube filled with

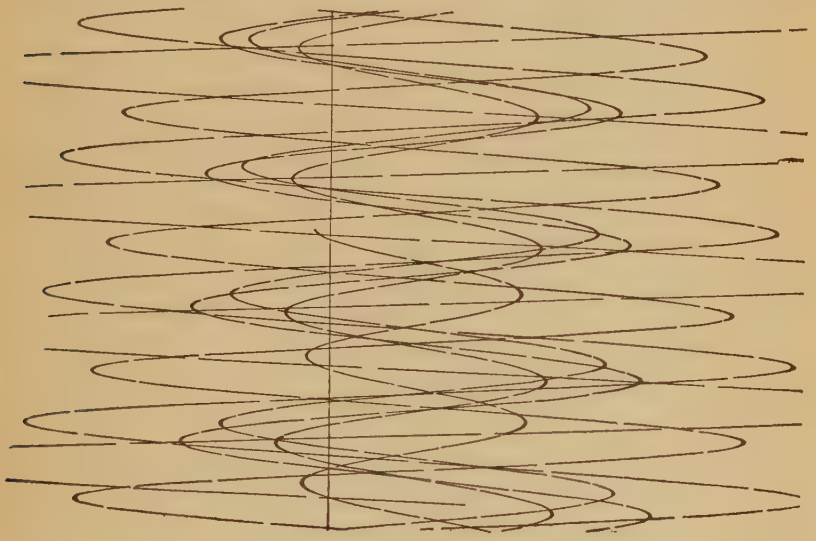


FIG. 115b

water, which was placed just in front of a narrow horizontal slit in the box enclosing the recording drum. By these devices the beam of light falling upon the drum produces only a single point of light. The distance from the slit to the mirror was about 90 cm. After each measurement a central reference line was marked upon the photographic paper by illuminating it from a specially provided point-source and turning the cylinder slightly with the hand. This central reference line, being parallel with the two bounding vertical planes of the drum, served as the line of reference in making measurements on the paper after its development (see Fig. 115b).

After many trials we finally hit upon the following device for regulating the time signals made on the recording paper by interrupting the recording light-beam. A clock provided with a pendulum was placed in the immediate vicinity of the slit just described. A thin vertical brass bar was screwed to the pendulum, so that it passed the slit twice with each complete oscillation of the pendulum. As the bar was blackened, so that there was no lateral reflection of light and the length of the pendulum was carefully regulated, the interruptions of the light-beam as recorded on the paper were very sharply defined. With the pendulum at rest its position was so chosen that the blackened bar did not extend completely across the slit, but left a narrow space at one side; by this adjustment the interruptions with each oscillation followed each other at 1/3 and 2/3 of the total period. This makes it easier to avoid subsequent errors in counting the gaps in the record curve. Since the period of the pendulum was about 3/4 second, the drum traveled through about 1 cm. between successive breaks in the curve. At a moderate drum velocity the crests of the record curve appeared to be about 120 mm. apart, on the average, and the interruptions about 0.2 mm., so that the time elapsed from one crest to the next of the sinusoid could be determined with great accuracy. Of course all time intervals were compared with a precise chronometer, so that they could be expressed accurately in seconds. The measured intervals were the mean of at least 25 full oscillations of the sphere in the liquid.[1]

The unmodified observations were checked by plotting the logarithms of the successive amplitudes against the time; if the observations were unaffected all points must lie in a straight line. By this means the logarithmic decrement δ could be measured with an accuracy of about 0.1 per cent.

A few preliminary experiments with liquids of known viscosities demonstrated to us the complete reliability of the method employed. At room temperatures the values of η for water, chloroform, and benzene were found to be

[1] For the details concerning these measurements, see *ov. cit.*, *Z. anorg. allgem. Chemie*, 175, 29f (1928).

0.01318, 0.006195, and 0.00777, respectively, while the literature gives for these values 0.01310, 0.00616, and 0.00780.

We then proceeded to study molten KNO_3, $NaNO_3$, $LiNO_3$, and NaCl. The data necessary for these measurements are illustrated in Table XXIV, which gives those relating to molten sodium chloride between 800° and 1000°. Further on we shall discuss our results with the perfected device.

The first measurements of the series were made on the nitrates of the alkali metals. After it had been verified that the heating current did not influence the damping effect either of the liquid or the air, if the inner heating element carried no current, the salts were carefully purified and the final measurements carried out. In the case of $LiNO_3$ we had great difficulty in eliminating the last traces of humidity from the molten mass: even at 100 degrees above its melting point this salt continued to give off water vapor. Commercial varieties of the salt are quite unsuited for such measurements, since they always contain impurities, we therefore prepared our material from the purest Li_2CO_3. The salt that we obtained was melted and the solidified mass dissolved in water; brown flakes that occasionally formed were filtered off, the salt again slowly melted, and kept at its melting point for a long time. It was then heated to about 100 degrees above its melting point and kept at that temperature until no further water vapor was given off.

Our difficulties in purifying this salt may explain why the results we obtained depart so markedly from those secured by other investigators, our values being not less than 18 per cent greater than those, for example, obtained for $LiNO_3$ by Goodwin and Mailey;[1] with the other salts, however, our results are generally in good agreement with the measurements by these two and by Lorenz and Kalmus.[2]

The results for sodium chloride given in Table XXIV are presented graphically in Figures 116 and 117.

[1] H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, **26**, 28 (1908).
[2] R. Lorenz and H. T. Kalmus, *Z. physik. Chem.*, **59**, 244 (1907).

TABLE XXIV.

Sodium chloride: NaCl.

Temperature	True logarithmic decrement	Time of oscillation	Moment of Inertia (C.G.S.)	Radius of the sphere		Coefficent of Internal Friction		Fluidity
°C	δ	(sec.)		(cm)	$d^{t}_{4^\circ}$	η_{obs}	η_{calc}	$1/\eta$
816	0.04308	8.93	107.36	1.004	1.539	0.01505	0.01494	66.93
818	0.04214	8.93	107.38	1.004	1.536	0.01457	0.01480	67.58
848	0.03875	8.93	107.45	1.004	1.519	0.01288	0.01286	77.76
852	0.03876	8.94	107.47	1.004	1.517	0.01284	0.01269	78.76
854	0.03873	8.94	107.48	1.004	1.516	0.01281	0.01257	79.55
864	0.03675	8.94	107.50	1.004	1.509	0.01179	0.01195	83.33
866	0.03652	8.94	107.51	1.005	1.507	0.01171	0.01184	84.46
868	0.03671	8.95	107.52	1.005	1.506	0.01181	0.01173	85.25
880	0.03615	8.95	107.54	1.005	1.499	0.01156	0.01118	89.44
880	0.03513	8.95	107.54	1.005	1.499	0.01105	0.01118	89.44
884	0.03487	8.95	107.55	1.005	1.497	0.01088	0.01099	90.99
900	0.03404	8.96	107.57	1.005	1.486	0.01053	0.01018	98.22
912	0.03196	8.96	107.60	1.005	1.479	0.00951	0.00962	103.8
913	0.03237	8.96	107.60	1.005	1.479	0.00997	0.00956	104.6
917	0.03147	8.96	107.61	1.005	1.476	0.00893	0.00942	106.2
921	0.03142	8.96	107.62	1.005	1.474	0.00926	0.00930	107.5
932	0.03073	8.97	107.65	1.006	1.467	0.00895	0.00888	112.5
956	0.02864	8.97	107.72	1.006	1.452	0.00803	0.00802	124.7
970	0.02729	8.98	107.75	1.006	1.443	0.00741	0.00763	131.0
987	0.02641	8.99	107.81	1.006	1.432	0.00760	0.00725	137.9
997	0.02617	8.99	107.85	1.006	1.425	0.00696	0.00708	141.2

The values of η can be computed with considerable accuracy by the formula $\eta = 0.12578 - 0.1805 \times 10^{-3}\, t + 0.02315 \times 10^{-5}\, t^2 - 0.03858 \times 10^{-9}\, t^3$; the logarithmic decrement in air, between 800° and 1000°, was about 0.00044.

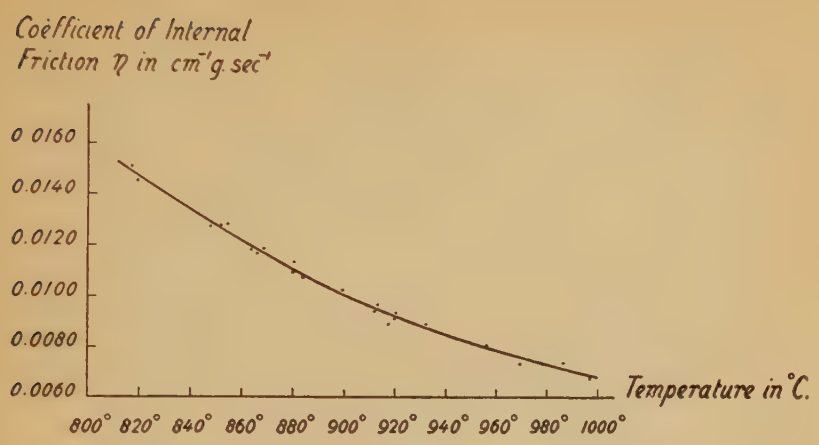


FIG. 116

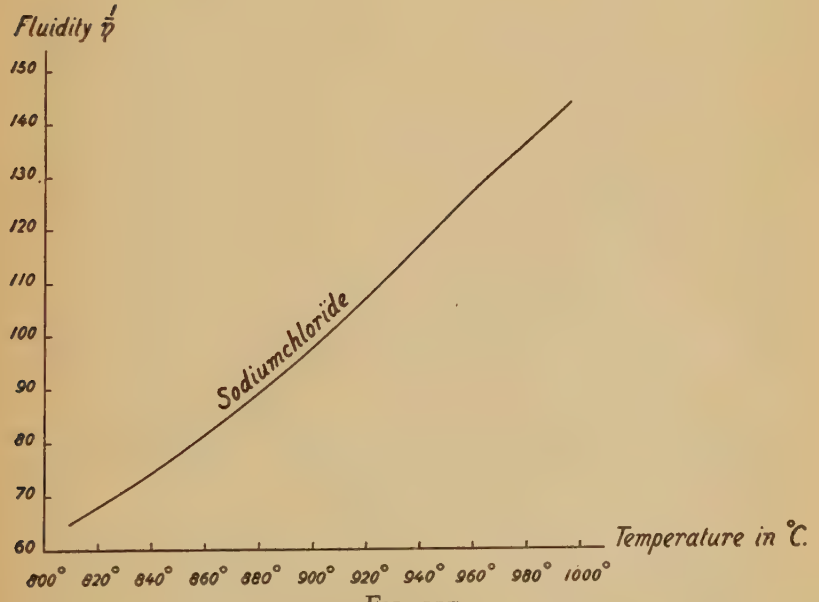


FIG. 117

The coëfficient of internal friction, η, for KNO_3 was determined between 348° and 542°; for $NaNO_3$ it was determined between 316° and 458°; while for $LiNO_3$ the

limiting temperatures were 260° and 429°. The results are expressed with great accuracy by the following equations:

KNO_3:

$$\eta = 0.16933 - 0.7418 \times 10^{-3}t + 1.88 \times 10^{-6}t^2 - 0.6533 \times 10^{-9}t^3$$

$NaNO_3$:

$$\eta = 0.20187 - 1.065 \times 10^{-3}t + 2.095 \times 10^{-6}t^2 - 14.40 \times 10^{-9}t^3$$

$LiNO_3$:

$$\eta = 0.31896 - 1.754 \times 10^{-3}t + 3.831 \times 10^{-6}t^2 - 3.23 \times 10^{-9}t^3$$

These results are shown graphically in Figures 118, 119 and 120, where they are also compared with those obtained by other observers. The fluidity $1/\eta$ is also represented graphically in Figure 121.

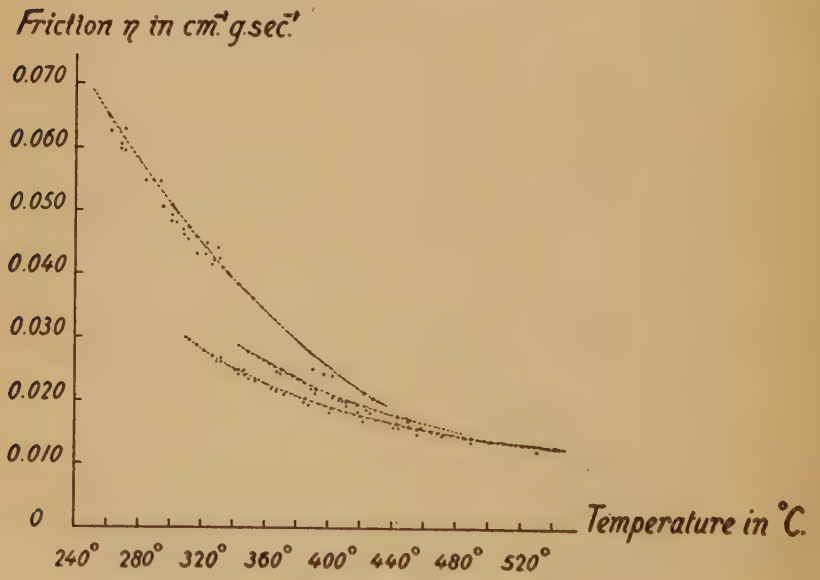


FIG. 118

In the case of the alkali nitrates investigated by us, we find no evident connection between the mutual positions of the curves and the atomic weights of the alkali metals; thus the values for $LiNO_3$ fall completely outside of those for KNO_3 and $NaNO_3$.

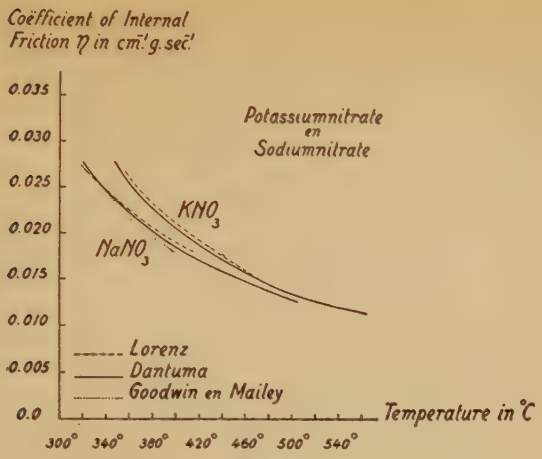


FIG. 119

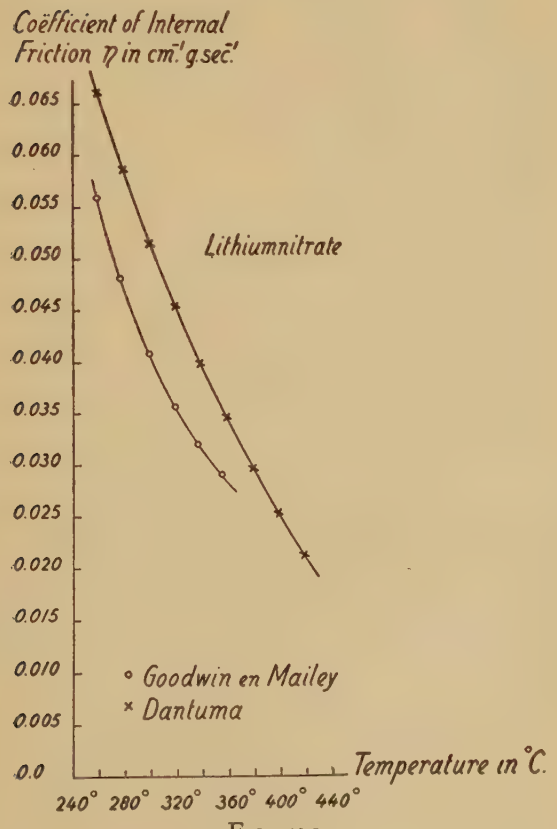


FIG. 120

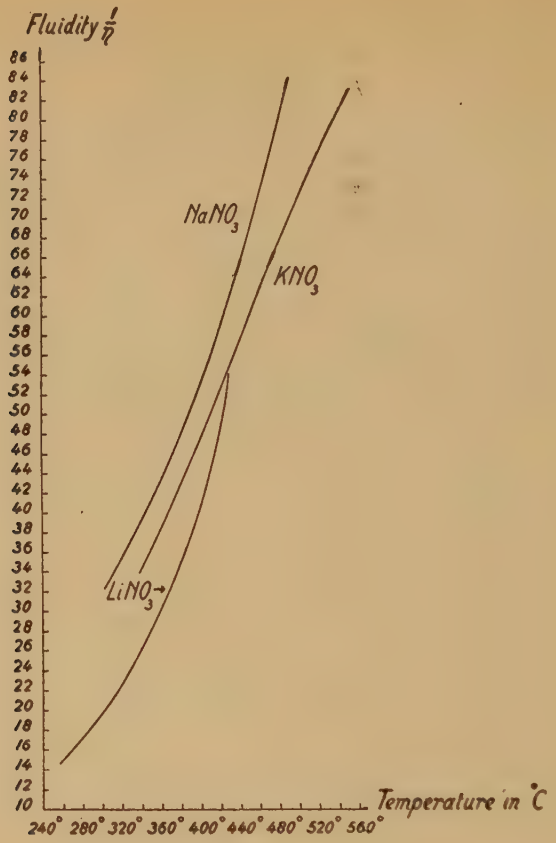


FIG. 121

In conclusion we may state that the method developed has proved to be reliable up to 1000°, and we do not doubt that it may also be applied at still higher temperatures. Its practical application remains difficult, and the determination of η, especially at high temperatures, is still a tedious task; but in the hands of a careful experimenter the method gives reliable results and to this extent the problem that we set ourselves may be considered solved.

CHAPTER XIX

The Precise Measurement of the Specific Heat of Solids up to 1650°C

Acknowledge of the relation between the specific heats of the elements and chemical compounds and their temperatures is of the greatest importance, both theoretical and practical. The theoretical considerations, viz., the changes in specific heat with temperature, at constant pressure, and particularly at constant volume, has roused the interest of both chemist and physicist during the past ten years. The conditions at lower temperatures have been specially investigated, but the whole problem has been discussed in the light of the most modern theories by a number of investigators, including Einstein,[1] Debye,[2] and Nernst.[3]

It is not my purpose to go into the details of the complicated theories regarding the relation between specific heat and temperature, nor to take up those discussions of the subject that are based upon the Planck quantum theory. It will be necessary, however, to review briefly the principal results of the same.

The specific heat of a substance can be determined at a constant pressure, c_p, and at a constant volume, c_v. The latter quantity is defined as the increase in the total energy, U, of 1 gm. of a substance when its temperature is raised 1° and its volume kept constant. Of course, under constant pressure the specific heat must be greater than this, because it is equal to c_v plus the caloric equivalent of the work done in opposition to the attractions between the constituent particles due to its thermal expansion, plus that done

[1] A. Einstein, *Ann. Physik*, (4)**22**, 180 (1907).

[2] P. Debye, *Ann. Physik*, (4)**39**, 789 (1912); R. C. Tolman, *Phys. Rev.*, (2)4, 145 (1914); M. Born and Th. von Karman, *Physik. Z.*, **14**, 15 (1913).

[3] W. Nernst and collab., *Sitzb. kgl. preuss. Akad. Wiss.*, 53, 247 (1910); *Ann. Physik*, (4)36, 49 (1911); etc.

against the external pressure. In the case of solid bodies, by far the greater part of this work is performed against those factors that oppose thermal expansion of the body. From a general equation in thermodynamics,[1] it can be deduced that:

$$c_p - c_v = \frac{0.02345(3\alpha)^2 T}{\kappa d},$$

where 3α is the coefficient of cubic expansion, T is the absolute temperature, κ is the compressibility of the body in kgm. per sq. cm., and d its specific gravity. It is thus possible to calculate C_v from the values of C_p as observed calorimetrically, provided 3α and κ be known at a series of temperatures. According to the older kinetic theory, the particles of a solid were considered as executing harmonic vibrations about certain fixed equilibrium positions under the influence of temperature, so that their kinetic energy at any moment is equal to their potential energy. From this theory it was deduced that the total energy U of a gram-molecule or gram-atom of any substance at the temperature T was equal to 3RT, assuming the so-called "equipartition of energy". From this it followed that C_v, being Ac_v, must be equal to $3R = 5.963$ cal. per gram-molecule, therefore being independent of the temperature. Since C_p averages 10 per cent greater, C_p, *i.e.* the "atomic heat" under constant pressure, should be about 6.4 cal. for each substance. This is the so-called "rule of Dulong and Petit", which they established in 1818 after measuring c_p; it states that the product of the atomic weight A and the specific heat c_p of each solid element differs very little from the average value of 6.4 calories.

It soon became evident, however, that the rule of Dulong and Petit could not be the expression of a rigorous law. A number of elements, such as C, B, Si, Be, showed atomic heats quite different from 6.4; it also gradually became clear that the atomic heat really is a function of the

[1] M. Planck, *Thermodynamics*, p. 118 (2nd Edition, Leipzig, 1905).

In general $c_p - c_v = -T(\partial v/\partial p).(\partial v/\partial T)^2$. Now $\kappa = -\frac{1}{v}\cdot\frac{\partial v}{\partial p}$ and $(3\alpha) = \frac{1}{v}\cdot\frac{\partial v}{\partial T}$.

If κ is expressed in kgm. per sq. cm., then since 1 kgm. = 98100 dynes, and 1 calorie = 4.183×10^7 ergs, it follows that the constant $\kappa = 0.02345$.

temperature. Weber proved, as early as 1875, that this occurred with precisely those elements whose specific heats increased rapidly with temperature. In recent years Nernst showed, by calorimetric measurements at very low temperatures, that all solid elements actually do behave like carbon, boron and the rest provided the temperature is low enough. The specific heats at the lower temperatures decrease very rapidly to values that approach zero as the temperature approaches Absolute Zero. Since that time physicists have taken a great deal of interest in the relation between specific heat and temperature, and various attempts have been made to find an explanation for this relationship and the true meaning of the Dulong-Petit rule.

Planck's development of the radiation theory and introduction of the "quantum of energy" into modern physics induced Einstein to give, in 1907, a theory of the specific heat as a function of temperature, deriving the well-known formula for the atomic heat C_v at constant volume:

$$C_v = 3R \frac{e^{\beta\nu/T} (\beta\nu/T)^2}{(e^{\beta\nu/T} - 1)^2},$$

where $\beta = Nh/R$, N being Avogadro's number and h Planck's universal proportionality factor, connecting the energy of a radiating particle with its frequency ν and R the gas constant. (In the CGS system, $\beta = 4.77 \times 10^{-11}$).

It is evident from this formula that C_v is a function of the temperature,[1] and approaches zero as T becomes zero. For very high values of T, however, the exponential factor approaches more and more closely to unity, so that C_v gradually approaches the value 5.963 if T increases.

This formula describes quite well the behavior, at low temperatures, of solids with reference to their heat capacity; but an analogous expression subsequently deduced by Debye does so still better. Debye's expression has a broader theoretical base and makes use of considerations relating to Planck's quantum theory. It may be stated, then, that the theory sufficiently explains the phenomena at low

[1] According to the old theory the total energy U of a body is given by U = 3RT, in the modern theory T is replaced by $\beta\nu/(e^{\beta\nu/T}-1)$.

temperatures, but does not serve so well for those manifest at very high temperatures. It is now perfectly certain that C_v at high temperatures generally does not approach a limiting value for 3R, but is often appreciably greater than that value—even at less extreme temperatures. This fact had already been established at lower temperatures for such metals as sodium and potassium and has often been correlated with their low melting points. The considerations to follow will make clear, however, that this phenomenon is a general one even at temperatures far distant from the melting point. It was not possible to prove this until we had developed a sufficiently accurate method for measuring specific heats at very high temperatures, so that even at 1650° there could no longer be a doubt of the reality of the phenomenon and the reliability of the observational results at such extreme temperatures.

In the United States work of high precision in high-temperature calorimetry has been done especially by White. His recent extensive monograph reviews the rich experimental material he has collected.[1] Since the method we have developed differs from his in many respects, and notwithstanding we have obtained results in full agreement with those obtained in Washington,[2] the reliability of both methods is clearly demonstrated and our claim of perfect reproducibility of the values redetermined is strongly corroborated. I think it will be of interest, therefore, to review the method we followed and the results obtained by it, the more so since we are sure that under favorable circumstances, even at very high temperatures, the determined values are accurate within 0.001 or 0.003.

The principle of the metal calorimeter was made use of here in the manner originally proposed by Nernst, Koref and Lindemann,[3] and as specifically applied to temperature measurements up to 900° by Magnus.[4] The construction of the apparatus profited by the experience of many investigators, more particularly that of White. All improve-

[1] W. P. White, *The Modern Calorimeter*. 194 p. (Chem. Cat. Co., New York, 1928).

[2] F. M. Jaeger and E. Rosenbohm, *Rec. trav. chim.*, **47**, 513 (1928).

[3] See *Sitzb. kgl. preuss. Akad. Wiss.*, —, 247 (1910); *Ann. Physik*, **36**, 49 (1911).

[4] A. Magnus, *Physik. Z.*, 14, 5 (1913); *Ann. Physik*, (4) 70, 303 (1923); A. Magnus and A. Hodler, *Ann. Physik*, (4) 80, 808 (1926).

ments that were found necessary as we went along have also been made, so that the instrument in its present state and our method of using it have now reached a very high degree of perfection.

The arrangement of the calorimeter, in its final form, is shown in diagramatic cross section by Figure 122. A double-walled vessel of thick wood had the inside dimen-

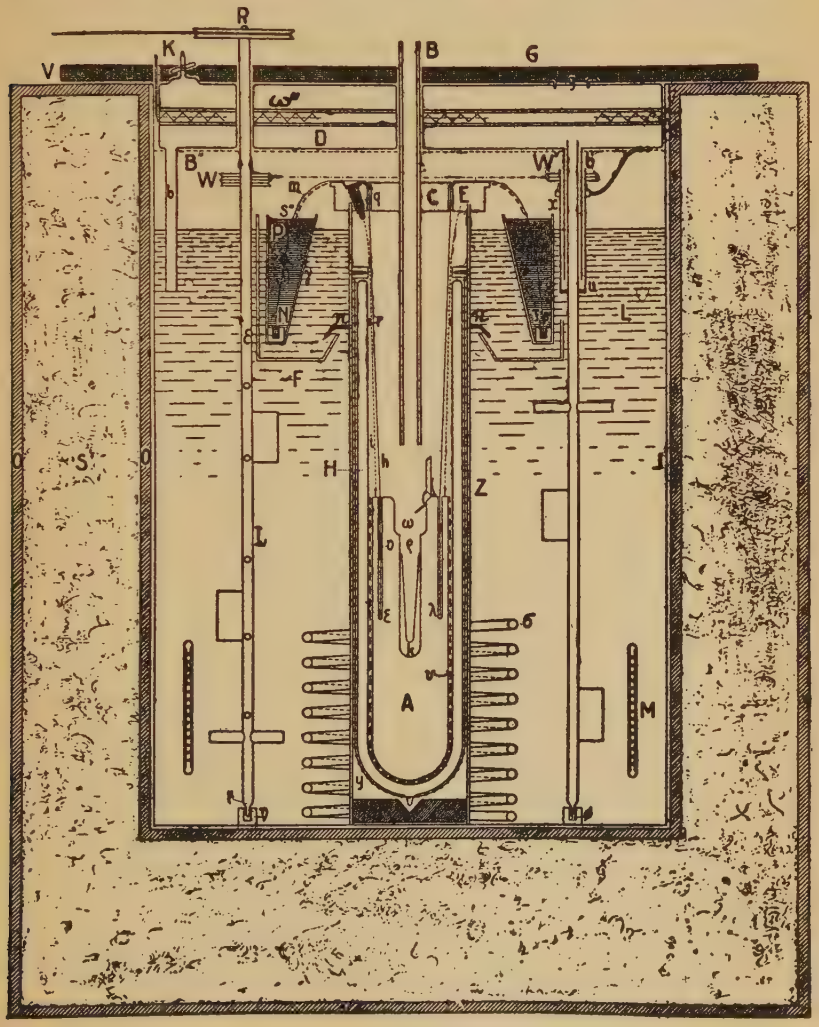


FIG. 122

sions 65 x 65 x 81 cm., and outside dimensions of 95 x 95 x 100 cm. (*O*, Figure 122). The space between the walls is completely filled with slag wool, *S*, which, in combination with the capacious water-filled reservoir placed inside it, serves to insulate the calorimeter from its surroundings. The water reservoir has a cover filled with water, and over this a layer of felt, *V*, several centimeters thick. The outside temperature also is kept as constant as possible. The water reservoir is formed by the galvanized iron vessel *J* which fits snugly into the vessel *O*, measuring 65 x 65 x 81 cm. This galvanized iron vessel contains the 260 liters of water surrounding the calorimeter and rising about 62 cm. from the bottom. It can be closed by a water-filled cover *D* supported on the iron rings *B″*. The cover is about 7 cm. thick and holds about 29 liters of water, which is forced up from the calorimeter vessel *J* and flows back into it in a steady stream. The water is maintained at a constant temperature by means of three heating-coils of nickel wire, *M*, which have been spread out in flat tightly-soldered brass boxes 0.5 cm. thick. The constant temperature is also controlled in part by a tubular coil, σ, through which cooling water circulates, and a large thermoregulator *Th* (Figs. 124 and 123). The stirring mechanism comprises three centrifugal stirrers, *l*, made of brass tubes 1.2 cm. wide provided with small holes and bearing cross-tubes at different heights. The tubes are about 20 cm. long and hurl the water out with some force when the stirrers are rotated. About 5 cm. above the water level wooden pullies *W* and *W′* carry driving belts made of spiral springs of brass wire; they are driven through the outside pulley *R* which is belted to an electric motor. The stirrers have steel points μ, resting in agate bearings, ϕ, on their lower ends; these bearings are fixed in brass blocks, η, firmly soldered to the floor of the vessel *J*. With this arrangement the stirrers work perfectly and without trouble after long service, and the water does not interfere in any way with the turning of the shaft ends in their bearings. The third stirrer, *W′*, is constructed somewhat differently as will be describde below.

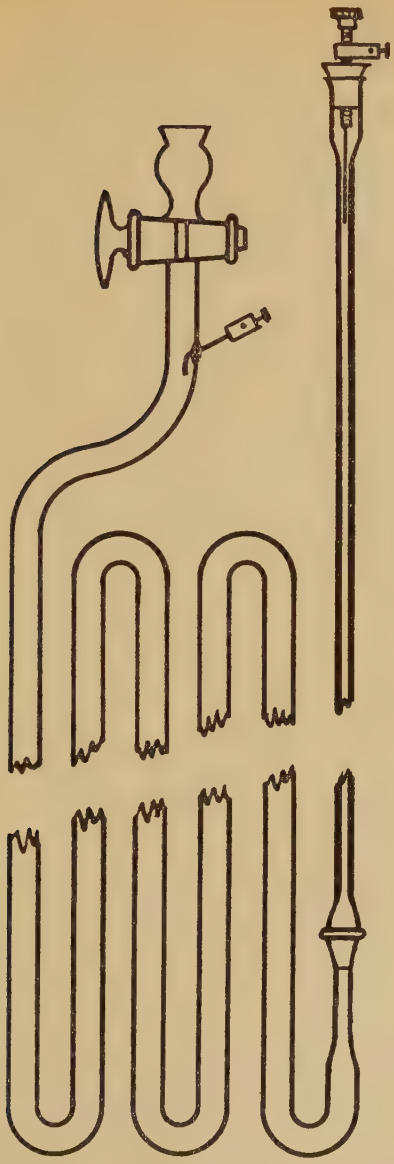


FIG. 123

For heating the water in the reservoir the heating coils *M* were employed, two of them being connected in series. By means of adjustable resistances, these coils maintain the water temperature at slightly below 20°. The third heating coil, however, is connected with the large thermoregulator *Th* shown in Figure 123. This thermoregulator consists of a glass tube folded on itself four times and terminating in a tube that narrows to a capillary; the regulator is entirely filled with six kilograms of pure mercury. A number of relays are connected to this regulator according to the wiring diagram of Figure 124.[1] In the thermoregulator it is essential to prevent as far as possible any induction-spark flashing when the contact between platinum pin and mercury thread is broken. This is secured by the system of relays shown diagramatically in Figure 124. By this arrangement the regulator was controlled by a very small fraction of the heating current (2 volts, 2 milliamperes) and any temperature oscillation above or below 20° was compensated almost immediately.

The tubular cooling coil, σ, also helped to bring about this result. An adjustable current of cold water flows slowly through the coil; the spiral rapidly absorbs the excess heat if the room temperature approaches too closely that of the calorimeter. The expansion of the mercury column in *Th* (Figs. 123 and 124) appears to be about 0.5 mm. per 0.001° change in temperature. Thus it was possible to maintain the temperature of the calorimeter water *L* constant within 0.001°, even when the experiments were prolonged, provided the water-filled cover *D* (Fig. 122) is also used. This cover was made of galvanized iron; the top is provided with an air-tight stopcock *K* that can be closed hermetically and a screw-cap *G* having a glass window *g*.

[1] In Figure 124 A_1, A_2 and A_3 represent three storage batteries; W_1—W_8 are adjustable and constant lamp resistances; R_1, R_2, and R_3 are relays. The circuit of battery A_2 is always closed on R_1 with a weak current. If R_1 turns to the right, the circuit through R_2 from A_1 is closed. In this case the circuit containing R_3 is broken, being the relay connected with the public power supply (220 volts). As a result of this interruption, W_2 is short-circuited, so that the current in the auxiliary heating coil S_1 is now increased. If the temperature of the water rises above 20°, however, the thermoregulator *Th* closes the circuit A_3. This carries a current that now is stronger than the current in A_2 and opposite in direction. This causes R_1 to turn to the left, thus breaking the circuit in which R_2 is inserted. This closes the contacts for the circuit containing R_3; resistance W_2 previously short circuited, is now again switched into the heating-current circuit, and the latter is now decreased; etc. etc.

The thick felt cover alone would not prevent small irregularities in the cooling of the calorimeter, even if the room temperature were kept constant. Therefore this cover was provided with a number of heating spirals w'' made of nickel wire surrounded by protecting tubes, and provided with a number of partitions that force the water to circulate in helicoidal paths within the cover.

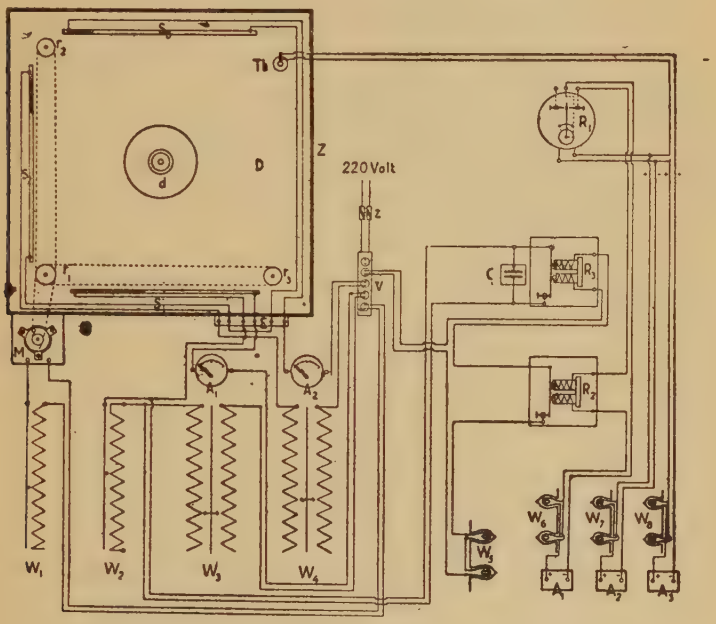


FIG. 124

In addition to the porcelain tube, B, which serves as an entrance for introducing objects into the calorimeter, and a tube at one side permitting the passage of the third stirrer, the cover has only the openings on its underside into which are tightly soldered the tubes b and b'. These tubes permit the water in the cover to communicate with that in the vessel J, so both tubes extend beneath the surface of the water L. The cover is filled by opening the stopcock K and connecting it with a suction pump; when the cover is filled K is closed and the third stirrer W' is set in motion, thus forcing the water from the cover into the thermostat while more water flows into the cover through

b. Having taken sufficient care, there is no longer an appreciable difference in temperature between the water in the cover and the water at *L*; so that the calorimeter is insulated upward as well as in other directions with respect to its surroundings. The wooden pulley *W'* of the third stirrer is not connected directly to the brass tube *b'*, but to a wider shorter tube *x* closed at the bottom by a perforated plate. This plate is fastened to the stirrer-shaft, so that the space between the cover and the thermostat is closed water-tight without calling for any ground-in junctions. A little space is left at *a*, between *L* and the cover, to permit the passage of the wire leads to the heating coils, etc. When the experiment is in progress *a*, in common with the whole calorimeter, is covered with a four-centimeter-thick layer of felt.

The calorimeter proper is placed in the constant-temperature region described above. A big Dewar vessel *H* is suspended by means of a strong silk net, *y*, in a cylindrically shaped vessel *Z*. The latter vessel is 70 cm. high, is loaded at its bottom with a thick layer of lead and is closed at the top by a ring of hard wood, *E*, saturated with molten paraffin and also by a wooden cover *C*. The Dewar vessel *H* is 42 cm. high and 11.5 cm. in diameter. It has its walls silvered on both sides. Between the wall of *Z* and the vessel *H* there remains a thin layer of air; within *H* and insulated from it by a thin layer of felt, *v*, is the calorimeter vessel proper.[1] This vessel consists of a cylindrical block, *A*, of pure aluminum weighing about 6000 gm., 27 cm. high and suspended by three strong silk cords, which together with the silk net, *y*, are fastened to the wooden ring *E*. The cords are constrained near the top of *H* by a wooden ring *r*. The aluminum block *A* has a diameter of 10.1 cm. and has 38 cylindrical borings, each 0.4 cm. in diameter and 16 cm. deep, arranged in two concentric circles. These bores accommodate 36 thermoelements of copper-constantan arranged in four series of 9 each. These series can be connected either in parallel or in series, as desired. The two remaining bores are used for two standard thermoelements,

[1] In later experiments the felt layer, *v*, has been replaced with a layer of soft "molecular" copper that is put on the market by Kahlbaum.

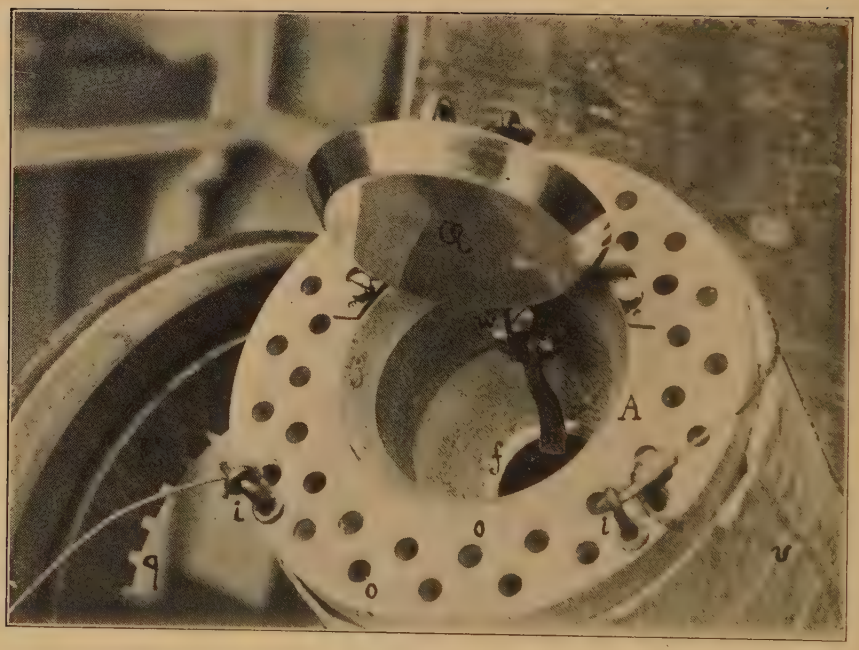


FIG. 125

while standardizing the other 36 elements; or to accommodate two supplementary sets of thermoelements connected in series, which serve to check any accidental extremely slight fluctuations in the temperature of the calorimeter water during the measurements. The plan of these borings is clearly shown by the photographic reproduction of the aluminum block *A* as viewed from above in Figure 125. Each bore is lined with a very thin-walled capillary of porcelain, *o*, fastened in the boring by means of fused Rose's alloy, thus providing direct metallic contact between the capillary and the aluminum block. The wires of the thermoelements, covered with a thin layer of a good insulating varnish, are inserted in these capillaries and fastened at the bottom by means of shellac, bringing the junctions at λ (Figure 122). The thermoelements have been properly standardized throughout their entire length by repeated heatings and coolings and treated further in the manner described by White.[1] The lead-wires *h'*,*h*, coming from the thermoelements in the calorimeter, are also well insulated. Where these wires leave the Dewar vessel, *H*, they pass through the openings, *q*, in the wooden ring *E*, which are filled with a mixture of wax and rosin. One must be careful that there are no kinks in these wires. Outside the ring these wires originally rested upon pieces of mica placed on the flat conical ring *s''*, made of perforated zinc plate. Subsequent experience showed that it is better not to use this ring *s''* at all. The second junction, ξ, of the thermoelements are placed in a ring of red copper, *N*, below the level of the water in the thermostat. This ring, 34 cm. in diameter, is made of bar copper 1.3 cm. x 1.9 cm. of rectangular cross-section. The thermoelement junctions also are inserted in thin-walled porcelain capillaries, β, sealed into 36 of the 38 borings of the copper ring *N* by means of Rose's alloy ϵ. When the other two borings are used to check the temperature of the water, they contain a series of thermoelements whose other junctions were placed in a Dewar vessel filled with pure ice. The ring *N* rests on the floor of a hollow frustrum-shaped jacket of sheet copper, γ, which is filled almost brim full of paraffin,

[1] W. P. White, *Physik. Z.*, 8, 337 (1907).

P. In order to maintain a perfectly constant temperature it proved necessary to surround the jacket, γ, with a cylindrical copper jacket, *F*, shaped as shown in Figure 122, with its central opening screened by the collar, π. It would be still better to place a second copper screen outside the jacket, *F*.

The temperature measurements were carried out by means of the thermoelements in the following manner. As described elsewhere,[1] all measurements were made by means of a potentiometer installation, that was quite free of thermoelectric contact potentials and supplied with five instead of the usual three decades. Potential differences smaller than those determinable with the smallest decade unit, were measured by means of the deflection of a calibrated galvanometer (of Zernike's design) which had a period of only two seconds at a critical resistance of 30 ohms and a sensitivity of 10^{-10} amperes. The working current of the potentiometer was so chosen that each unit of the compensator corresponded to 2000 μv; in the final measurements the galvanometer deflections were always measured both to the right and to the left by means of a reversing switch free of all contact potentials, that controlled the direction of the current in the compensator. A very weak current always circulated in the bank, so that no measurements were started until there was absolute certainty that the temperature of the resistance coils would remain notably constant. The complete compensation of the instrument was always rechecked before each measurement.[2]

The four pairs of wires connecting the four series of thermoelements with the potentiometer were well insulated and brought out of the calorimeter through the opening *a*. They were fixed side by side in a reservoir filled with frozen paraffin. They were then passed over glass rods provided with mica rings and thence connected with the measuring apparatus. We used the same compensator we employed when measuring the furnace temperature by means of the platinum-Pt-Rh thermocouple. In order to

[1] F. M. Jaeger, *Anleitung*, p. 14.

[2] On moist days it was desirable to force a slow current of carefully dried air through the potentiometer box, in order to remove the water vapor that condensed on the coils.

prevent any leakage of the electric heating current supplying the electric resistance furnaces, into the measuring apparatus, we found it necessary to adopt White's suggestion[1] and place all measuring instruments on grounded and interconnected metallic plates.

As remarked before, all temperatures have been reduced to the scale of the Washington nitrogen gas thermometer as fixed by Day and Sosman. The platinum-Pt-Rh thermocouples were calibrated against a standard element standardized in Washington, or by determining a series of characteristic and well-known melting points.[2] The alternate readings of the thermoelement in the calorimeter and in the furnace, and the connection (series or parallel) of the four groups of thermocouples in the calorimeter, were obtained by means of specially made plug switches that were practically free from contact potentials and accessory resistances. Any disturbances of this nature could always be eliminated also by reversing the working current in the compensator, as mentioned above.

The calibration of the copper-constantan thermocouples in series of nine elements, showed that all the elements were practically identical and perfectly insulated within the calorimeter. Each set of nine elements showed the temperature, t, as a function of the electromotive force, E, expressed by the equation $t = 0.00379698E - 0.000,000,006,29E^2$, when t is in degrees centigrade and E is in microvolts. From this relationship it follows that between 19° and 23°, or within the limits of the variations in temperature of the calorimeter, a difference in potential of $1\mu v$ corresponds to a temperature change of 0.002703° for each set of thermoelements. If all the elements are connected in series, as usually, a potential-difference of $1\mu v$ corresponds to 0.000676°. It seems, therefore, that it is possible to determine with certainty temperature-differences of 0.0001°C.

In the center of the aluminum block, *A*, is bored an opening 5 cm. in diameter, which soon decreases rapidly

[1] W. P. White, *Phys. Rev.*, (2) 8, 337 (1907).

[2] The melting points employed were: $NaNO_3$ (308°); NaCl (800°); Li_2SiO_3 (1201°); artificial diopside (1391°); artificial anorthite (1551°); $BaSiO_3$ (1604°). Corrections of the thermoelement K: at 308° $+10\mu v$; 800° $-13\mu v$; 1201° $+6\mu v$; 1391° $+23\mu v$; 1604° $+56\mu v$.

to a cylindrical bore of about 2.7 cm. The lower portion of this smaller bore is nicely fitted by a piece of aluminum, *k* (Fig. 122), whose steep conical bore has a lining of 0.35 mm. platinum reaching from the base of the conical bore to above the inner narrowing, where the lip of the platinum lining is turned down against the aluminum, as shown at *f*, Fig. 125. This platinum lining weighs about 120 gm. The device of making this bore conical as at *k*, Fig. 122, insures a much better contact between the calorimeter wall and the hot body introduced. In the original design the hot body was caught on a platinum sheet supported by a tungsten spiral. The new design has reduced the time required to restore the normal temperature gradient of the calorimeter, after introducing the heated body, from several hours to a half-hour; while the maximum temperature is attained in about eight seconds—even for platinum heated to 1600°—instead of after a lapse of several minutes. With a new and better-fitting platinum lining for the calorimeter bore the heat conduction was so improved that it was finally possible—when the hot object was a metal[1]—to complete the total delivery of the heat of the hot object within a few seconds. This was so rapid that it was not even possible to follow the change from the initial increase up to its maximum, by means of the switch-gear of the potentiometer.

The heated body falling into the opening ω (Figs. 122, 126) first strikes and releases the extremely sensitive trigger *n*, which releases the nickel lid, *Q*, and this driven by the strong steel spring *V'* closes the opening ω in the shortest possible instant. This mechanism, which works like a mouse trap, is clearly shown in detail in Figure 126.

The porcelain tube *B* (Figure 122) which passes through the water cover *D*, is firmly fixed in the wooden lid *C* of *Z*. This tube *B* forms the passageway for the heated object into the channel of the calorimeter.

The substances to be tested were heated in electric resistance furnaces supplied with platinum coils wound on their inner walls, and of the type always used in the

[1] In the case of poorer conductors, as water or porcelain, the complete heat delivery lasted somewhat longer.

Groningen Laboratory.[1] These furnaces were screened as far as possible with double-walled detachable water-jacket screens and bases through which cold water was continually flowing. Thus we prevented as far as possible heat loss from the furnace to the felt jacket and thence inward.

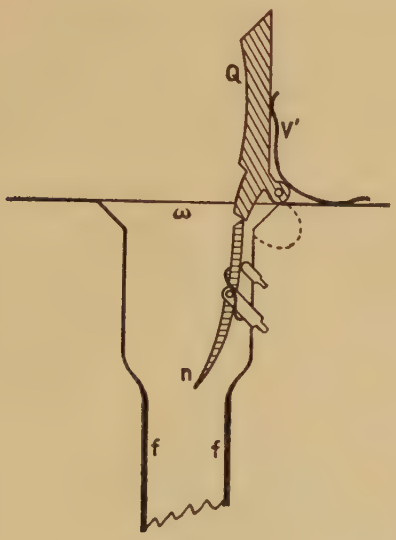


FIG. 126

The accompanying Figure 127 shows the construction of these furnaces. The furnace proper stands on the iron frame *W* whose three legs *w* support it on the iron table *T*, and this in turn rests by means of its legs *t* upon the solid base-plate *B*. The latter moves on iron rollers running on a pair of rails. The water-jackets, all intercommunicating, are indicated by *M*. The furnace *UECD* is composed of chamotte parts kept together by circular iron plates, *nn'*, and stove bolts (not shown). The furnace core *O* is of hard magnesite with a coil of 1.3 mm. platinum wire wrapped about its inside wall. The filling *S* between the core and the fire brick is calcined magnesia. The Marquardt-tube *GG'* has its lower portion surrounded by a water-screen *P* which is kept in contact with *G* by an elastic metal collar *r*. The water-screen *Q* closes *G* at the bottom. This screen

[1] F. M. Jaeger, *Anleitung*, p. 37.

swings on the hinge e under the action of a spiral steel spring σ, and at any time—when the crucible is detached from its suspension within the furnace—can be drawn aside by the cord V, being returned to its original position almost instantly when V is released. H is the tube leading into the calorimeter. The cooling due to P and Q is so effective that the water escaping through the pipe b_2 remains perfectly cold, and there is no appreciable radiation to the calorimeter even when the furnace has reached

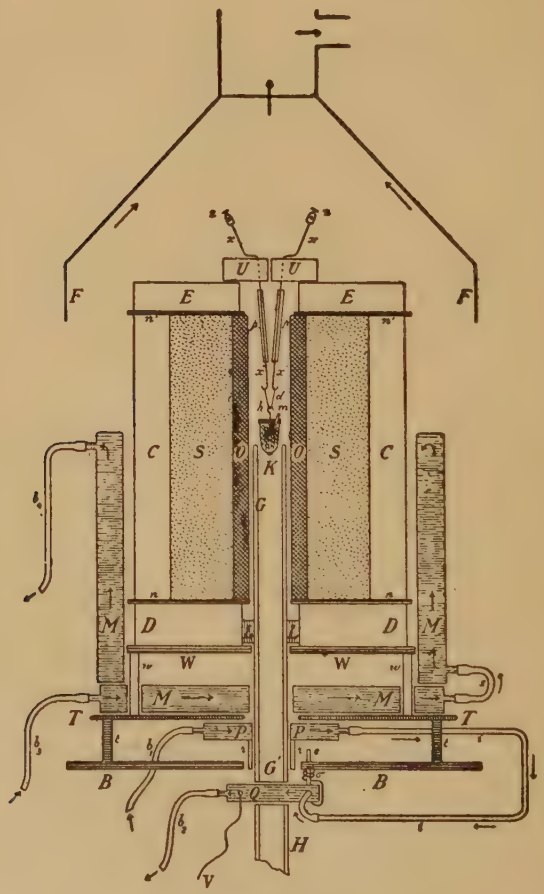


FIG. 127

1625°.[1] The fire brick ring *U* is in two parts, which permits the suspended system *px'K* to be exactly centered in the furnace at any temperature position. The very feeble currents of hot air still rising along the furnace walls were readily nullified by permitting them to escape by a ventilator flap. An undesirable heating of the room, by the heat developed in the rheostats controlling the furnace current, was prevented by inclosing them in a wooden jacket from which the heated air was carried off by a line of pipe. Great care was also taken to keep the room temperature as nearly as possible at 20° day and night by partly turning off the general heating system and warming the room by means of a gas oven provided with a large thermoregulator. The resistance furnace had been mounted on detachable iron rails above the calorimeter; and from its remote position under the ventilator, at the desired moment, a single pull would bring it quickly and exactly in position over to *B* (Figure 122). It could be returned to its original position with equal ease. In the course of our measurements, however, it appeared that the very perfect insulation of the furnace and of the calorimeter made it unnecessary to remove the furnace from above *B*; so that occasionally it was permitted to remain in its place after necessary precautions were taken.

The objects were suspended, by a thin platinum wire, in a platinum vessel in the furnace within its constant temperature region; this platinum wire was melted instantaneously by passing a strong electric current through it at the moment when the object was to be dropped into the calorimeter. Depending on the nature of the substances under investigation, it was necessary occasionally to inclose these substances in a vessel of hard porcelain placed within the platinum vessel. For this reason the specific heats of both the porcelain and the platinum had to be accurately determined. We shall have occasion to refer to this arrangement when describing our measurements.

For determining the water-equivalent of the calorimeter and standardizing the thermocouples, a double-

[1] This fact may be checked by the variation in the time of falling of the heated object. This time usually did not exceed 0.05—0.1 second. We determined the correction applicable for this source of error and found it to be quite negligible.

walled copper air bath well insulated with asbestos and felt, was employed. In this it was possible to produce, by electric heating, water vapor whose temperature depended upon the momentary atmospheric pressure. It required about three-quarters of an hour for the object within the air-bath to assume perfectly the temperature of the same, as determined by a thermoelement touching the platinum vessel or placed within its center. This heating apparatus also worked very satisfactorily, when the necessary precautions were taken.

Determination of the water-equivalent and of the cooling constant k *of the calorimeter.*

Having determined the normal temperature march of the calorimeter and introduced the heated object into the same at the moment τ_0, at first the temperature rises rapidly; it then falls and when all the added heat has been given off, the normal rate of cooling of the calorimeter is re-established. When the calorimeter employed contains a liquid, so that the heat is delivered rapidly and equally by continued active stirring, the temperature X at the moment τ_0—which the calorimeter would have attained instantly if there were an infinitely rapid exchange of heat between the hot object and the instrument—can be found by a well-known simple graphic extrapolation of the cooling curve. In a metal calorimeter, where stirring is not possible, the maximum temperature *C* will be reached within a short interval that depends on the thermal conductivity of the metal, the position in the metal block where the thermo-elements have been located, and on other factors. The curve giving the temperature T as a function of time (Fig. 128) can be regarded as consisting of two parts: the "normal" portion *DE* and the "abnormal" portion *BCD*. If the curve *AB* represents the temperature march of the calorimeter before the heated object is introduced, the problem is to substitute for the "abnormal" section *BCD* the "normal" curve P_1X which must be regarded as the section of the normal cooling curve adjoining *DE*. In this case X represents the required value of the calorimeter temperature at the instant τ_0 as a mere consequence of the heat emitted by the heated object.

Since the thermoelements have been placed half-way between ω (Fig. 122) and the outer wall of the metal block A, the maximum temperature C is always higher here than the true temperature X.

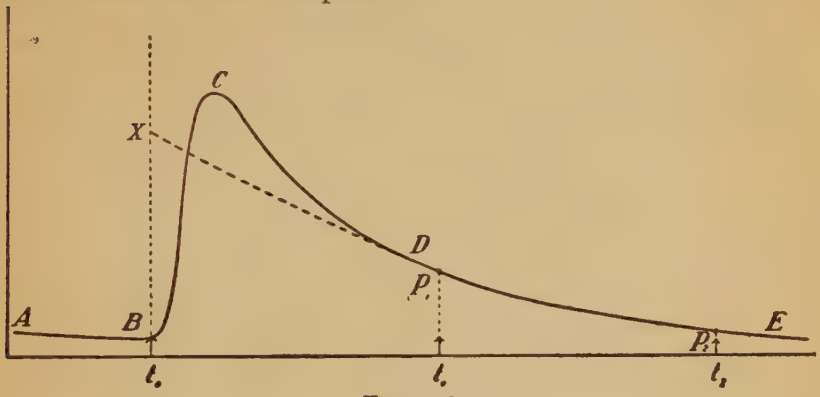


FIG. 128

According to the method of Magnus, which we extended somewhat, this temperature X may be found as follows. It is reasonable to assume that:

1. The mean value of the temperature of the water surrounding the calorimeter remains constant for a long time; and

2. The loss of heat by the calorimeter as a whole depends, at any moment, solely on the difference in temperature between the calorimeter and the surrounding water, this loss of heat being always directly proportional to that difference in temperature.

Then, if e is the EMF of the thermocouples, and τ the time, we have:

$$-\partial e/\partial \tau = ke$$

If at the time $\tau = 0$, the heated object is introduced into the calorimeter, it follows that:

$$-\int_0^{\tau} \frac{\partial e}{e} = k\tau .$$

Therefore,

$\log_{10} e_0 - \log_{10} e_\tau = 0.4343\ k\tau$, e_0 being the EMF of the thermoelements at the time $\tau = 0$.

From this it follows:

$$\log_{10} e_0 = \log_{10} e_\tau + 0.4343\, k\tau = \log_{10} e_\tau + k'\tau.$$

To find the cooling constant, $k' = 0.4343k$ of the calorimeter, we measured the EMF e_{τ_1} and e_{τ_2} at the moments τ_1 and τ_2, after the cooling rate of the instrument had returned to "normal", that is, after the point D (Fig. 128) had been passed.

From $$-\int_{\tau_1}^{\tau_2} \frac{\partial e}{e} = \int_{\tau_1}^{\tau_2} k\,d\tau,$$

it follows:

$$k' = 0.4343k = \frac{\log_{10} e_{\tau_1} - \log_{10} e_{\tau_2}}{(\tau_2 - \tau_1)}.$$

Five series of preliminary experiments, which were extended over intervals of 16 to 20 hours, gave us in this way, for k' the successive values 0.0006746, 0.0006744, 0.0006742, 0.0006741, and 0.0006742 μv per minute. This shows that, with the above described arrangement of the apparatus, k' may be regarded as practically constant at the mean value of 0.0006743 μv per minute, even over long intervals of time. Later on, when all necessary improvements in the apparatus had been made, eliminating all possible temperature differences between the water in the cover and the water in the vessel J, we found a somewhat larger value for k', viz., about 0.000702 μv per minute.

At each measurement we determined the value of k' by measuring e_{τ_1} and e_{τ_2} at 10-minute intervals after the moment when the normal march of the calorimeter had been re-established.

The manner in which the water-equivalent, W, for the calorimeter was determined may be illustrated by the following, the data having been determined before we adopted the final improved platinum lining for the block. An adequate, precisely measured amount of pure water was placed in a small, conical platinum crucible that fitted accurately into the conical bore k of the calorimeter. The crucible was closed by means of a platinum cover tightly

soldered to it with silver, and a small platinum filling-tube as well as a small hook were fastened to this cover.

Weight of platinum = 10.8192 gm.,
Weight of silver = 0.0562 gm.,
Weight of tin = 0.1408 gm.,
Weight of water = 5.9564 gm.,

The water-equivalent of the whole crucible was therefore equal to $(10.8192 \times 0.032 + 0.0562 \times 0.055 + 0.1408 \times 0.044 + 5.9564) = 6.3125$ calories per degree.[1]

The crucible was suspended, by means of a thin wire, in the copper air bath described above; it was heated by means of water vapor and, after a constant temperature had been attained, it was suddenly released by a special mechanism and caught in the calorimeter where the temperature was observed at regular intervals.

In Table XXV the electromotive forces of the thermocouples are indicated by e′, and must be multiplied by 2000 to reduce them to microvolts.

From the values of e′ (0.2923 and 0.0463) we may calculate the value of k′ of the temperature X at 2h 11m, and the value W.

Calculation of k′. The above values of e′ correspond to e_{τ_1} and e_{τ_2} of 584.6 μv and 92.6 μv, respectively; $(\tau_2 - \tau_1)$ being 1140 minutes. From these values it follows that k′ = 0.0007020 μv per minute.

To find e_{τ_0} from e_{τ_1} = 584.6 μv, it must be remembered that 34 minutes have elapsed between the two values. To find the increasing temperature at the instant τ_0, it must be remembered that at 2h 11m the temperature of the calorimeter was 99.5 μv above that of the surrounding water (20.067°).

Therefore, $\log_{10} e_{\tau_0} = \log_{10} 584.6 + 34\ k' = 2.76686 + 0.02387 = 2.79073$; therefore, $e_{\tau_0} = 617.3$ μv, corresponding to $617.3 \times 0.000676° = 0.4175°$. At the instant τ_0 the temperature of the calorimeter = 20.4845°, while the increase in the temperature of the instrument was $(617.3° - 99.5°) \times 0.000676° = 517.8 \times 0.000676 = 0.3503°$.

Therefore the platinum crucible has undergone a decrease in temperature from 100.096° to 20.4845°, corresponding to a delivery of heat equal to 79.6115×6.3125 calories = 502.547 cal. Since the instrument increased in temperature by 0.3503°, as a result of this heat delivery, the water-equivalent W of the calorimeter is equal to 502.575 : 0.3503 = 1435.1 cal.

[1] Here, and in what follows, our unit is always the mean gram-calorie. This unit is easily converted into other units if desired.

TABLE XXV.

Electromotive forces (e′) *of the Thermocouples*

(e′ × 2000 = EMF in μv.)

Time:	Electromotive Forces observed: e′ (*to the right*):	e′ (*to the left*):	
P. M. 1 hr. 59½ min.	0.0498	—	
2 hr. 0 min.	—	0.0496	
2 hr. ½ min.	0.0498	—	
2 hr. 4½ min.	—	0.0496	Mean value: 0.04975
2 hr. 5 min.	0.0499	—	
2 hr. 5½ min.	—	0.0496	
2 hr. 9½ min.	0.0499	—	
2 hr. 10 min.	—	0.0496	
2 hr. 10½ min.	0.0499	—	
2 hr. 11 min.	←The crucible is introduced into the calorimeter		
2 hr. 15 min.	—	0.2729	
2 hr. 20 min.	0.3068(max.)	—	
2 hr. 25 min.	—	0.3046	
2 hr. 30 min.	0.3010	—	
2 hr. 35 min.	—	0.2976	
2 hr. 39½ min.	0.2952	—	
2 hr. 40 min.	—	0.2947	
2 hr. 40½ min.	0.2946	—	
2 hr. 44½ min.	—	0.2924	Mean value: 0.2923
2 hr. 45 min.	0.2923	—	
2 hr. 45½ min.	—	0.2919	
(After 19 hours):			
A. M. 9 hr. 44½ min.	0.0465	—	Mean value: 0.0463
9 hr. 45 min.	—	0.0461	
9 hr. 45½ min.	0.0465	—	

Reduced barometric pressure = 762.66 mm. (0°)
Boiling point of water = 100.096°C.
Temperature of crucible = 100.07°
Correction for mercury thread = + 0.03
True temperature of crucible = 100.10°
Temperature of surrounding water = 20.067°

In a series of such experiments with the above instrument, as finally perfected, the determined values of the water-equivalent W did not differ from one another by more than 0.07 per cent. The improvements in the water-filled cover fully met the conditions mentioned above, and the very slightest oscillations in temperature were eliminated. After we adopted the aluminum cone *k* and the new platinum lining for the inner bore of the calorimeter, redeterminations of W in seven series of experiments gave the following values: 1417.2, 1417.9, 1418.7, 1417.0, 1417.9, 1417.8, and 1418.8 calories. Their mean gives W = 1417.9 ± 0.9 cal. The deviations are not greater than +0.063 per cent, a degree of accuracy that is more than sufficient. We therefore adopted this value in all subsequent measurements. The apparatus employed has now been in use for a long time and has given excellent results in all respects.

We first determined the specific heat of pure platinum. Our material was of the purest, free from iridium, being such as Heraeus uses for thermocouples and resistance thermometers. A crucible of this metal (See Fig. 127, *K*) was provided with a tube, *m*, cover, hook, *h*, as described, and the crucible filled with ten or twelve small spheres of the same metal, the total weight of the platinum being 52.7 gm. The thermocouple was inserted into the crucible through the tube and the junction adjusted to the center of the crucible. The whole was suspended in the constant-temperature region of the furnace, by means of an iridium-free platinum wire *d*, and heated to the desired temperature. After remaining at this temperature for a long time, the wire *d* was suddenly melted at its lower end by means of a very strong electric current introduced at the contacts *z* through the 2 mm. platinum wire *x*. The crucible thus released fell through the Marquardt-tube *GG'* and was caught in the calorimeter. The weight of the crucible was redetermined after each temperature measurement, because eventually the melting wire *d* caused traces of liquid platinum to fall on the cover, and also because there is always some danger, at very high temperatures, of a loss of weight by the crucible due to a slight volatilization of the metal

in the presence of the atmospheric oxygen. The results of the determination of the specific heat of pure platinum are collected in Table XXVI where they are compared with those obtained by White, who worked with material from another source and employed a different type of apparatus (liquid-containing calorimeter).[1] The values of c_p here compared were calculated by White's formula, viz., $c_p = 0.03175 + 0.0000032\,t$. The values of Q, representing the total amount of heat delivered between t° and 20°, are computed from our measurements. For values of these quantities between t° and 0°, we used Gaede's determinations of c_p,[2] which Magnus[3] finds can be represented by the equation $c_p = 0.031054 + 13.6 \times 10^{-6}t - 0.028 \times 10^{-6}t^2$.

From this equation we deduced for $\int_0^{20} c_p dt$ the value 0.62373, so that the mean value of c_p between 0° and 20° is found to be 0.031186. The values Q_0 in the next column are calculated in this way from the values of Q; and the values Q'_0 of the following column have been computed from three determinations of Q_0, *e.g.* at 301°, 933° and 1546°, by means of the formula $Q'_0 = 0.03162t + 0.00000308625t^2 + 0.000000000077751t^3$, which gives a very excellent representation of the values of the total amounts of heat delivered between t° and 0°.

The true specific heat, c_p, at each temperature can then be calculated by the equation

$$c_p = dQ'_0/dt = 0.03162 + 6.1725 \times 10^{-6}t + 2.3325 \times 10^{-10}t^2.$$

This formula cannot be used below 150°; it is true that at that point the deviations are still small, but they are considerably larger than the degree of accuracy obtainable, which is about 0.1 per cent.[4]

The values we obtained for the true specific heat at a constant pressure, up to 1620°, are represented graphically

[1] W. P. White, *Phys. Rev.*, (2) 12, 436 (1918).

[2] W. Gaede, *Physik. Z.*, 4, 105 (1902).

[3] A. Magnus, *Ann. Physik*, 48, 998 (1915).

[4] Magnus computed the true specific heat, c_p, between 130° and 850° by means of the linear function $c_p = 0.03159 + 5.8568 \times 10^{-6}t$. The temperature interval which we are considering has about double the extent of the one Magnus discussed, and the curve departs considerably from a straight line; we have therefore preferred to make use of an equation having 3 constants.

Table XXVI

Mean and True Specific Heats under Constant Pressure for Platinum between 0° (respectively: 150°) and 1604°

Temp. t (corr.)	Final temp. of calorimeter and platinum	Δt observed	Weight G of the heated platinum:	Mean specific heat $\bar{c}_p$:	Mean specific heat (White): $\bar{c}_p$	Total amount of heat delivered for 1 gm. of Pt. (calories) Q $t°-20°$	Q_o $t°-0°$	Q'_o $t°-0°$	True specific heat c_p at $t°$
°C	°C	°C	gm.				(obs.)	(calc.)	
100	20	—	—	—	0.03186	—	—	—	—
210.7	20.35	0.22994	52.712	0.03247	0.03242	6.1808	6.8154	6.800	0.03293
300	20	—	—	—	0.03271	—	—	—	—
301.05	20.59	0.33984	52.709	0.03265	0.03271	9.1572	9.7993	9.8008	0.03350
408.3	20.62	0.47467	52.706	0.03299	0.03305	12.7900	13.4330	13.4300	0.03418
500	20	—	—	—	0.03333	—	—	—	—
504.8	20.81	0.59864	52.742	0.03330	0.03336	16.1172	16.7662	16.7583	0.03479
577.9	20.93	0.69352	52.734	0.03353	0.03360	18.6750	19.3277	19.3183	0.03526
700	20	—	—	—	0.03399	—	—	—	—
707.4	20.91	0.86486	52.714	0.03393	0.03401	23.2926	23.9447	23.9471	0.03610
747.8	21.14	0.91930	52.717	0.03406	0.03414	24.7500	25.4093	25.4039	0.03637
869.1	21.04	1.0844	52.742	0.03445	0.03453	29.2140	29.8701	29.8632	0.03716
900	20	—	—	—	0.03460	—	—	—	—
933	21.39	1.1734	52.737	0.03464	0.03473	31.5786	32.2457	32.2504	0.03758

TABLE XXVI (Continued)

Mean and True Specific Heats under constant Pressure for Platinum between 0° (*respectively:* 150°) *and* 1604°

Temp. t (corr.)	Final temp. of calorimeter and platinum	Δt observed:	Weight G of the heated platinum:	Mean specific heat $\bar{c}_p$:	Mean specific heat (WHITE): $\bar{c}_p$	Total amount of heat delivered for 1 gm. of Pt. (calories) Q $t°-20°$	Q_o $t°-0°$	Q'_o $t°-0°$	True specific heat c_p at $t°$
°C	°C	°C	gm.				(obs.)	(calc.)	
945.7	21.33	1.1903	52.722	0.03468	0.03477	32.0576	32.7228	32.7286	0.03767
1068	21.70	1.3625	52.725	0.03507	0.03516	36.6942	37.3709	37.3849	0.03840
1100	20	—	—	—	0.03523	—	—	—	—
1109.8	21.60	1.4238	52.749	0.03522	0.03530	38.3200	38.9936	38.9989	0.03876
1218	21.80	1.5817	52.743	0.03559	0.03565	42.5670	43.2469	43.2324	0.03948
1300	20	—	—	—	0.03592	—	—	—	—
1302	21.97	1.7057	52.755	0.03588	0.03599	45.9260	46.6111	46.5724	0.04005
1309	21.91	1.7162	52.752	0.03589	0.03594	46.1933	46.8514	46.8526	0.04010
1374	21.96	1.8137	52.767	0.03610	0.03614	48.8079	49.4675	49.4741	0.04054
1464	22.17	1.9509	52.795	0.03637	0.03643	52.4400	53.1314	53.1498	0.04116
1546	22.27	2.0721	52.736	0.03665	0.03670	55.8445	56.5390	56.5467	0.04172
1604	22.41	2.1653	52.704	0.03685	0.03688	58.2830	58.9819	58.9790	0.04212

The true specific heat at $t°$ between 150° and 1604° was calculated from the equation:

$$c_p = 0.03162 + 6.1725 \times 10^{-6}\, t + 2.3325 \times 10^{-10}\, t^2.$$

in Fig. 129; the same figure compares those from White's measurements up to 1300° and those for corresponding temperatures as obtained by Magnus. Although White employed a different apparatus—for which he claims an accuracy of about 0.3 per cent—his values are almost identical with ours. The greatest differences lie between 950° and 1100° and are not greater than the degree of uncertainty mentioned, 0.3 per cent, while for the remainder of the range they do not exceed 0.15 or 0.20 per cent of the

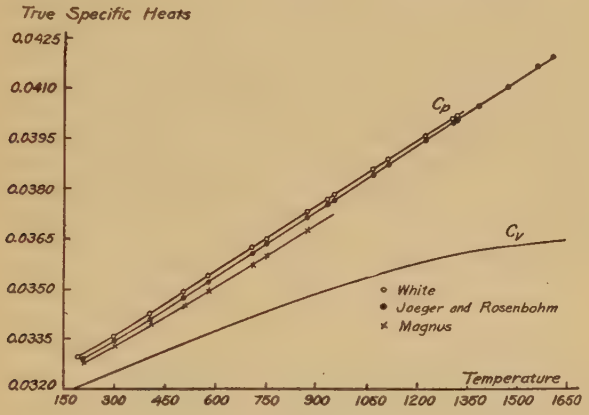


FIG. 129

total values. This complete accordance in the two sets of results may be regarded as a proof of the accuracy of our method and of our results. Contrary to White's straight line for representing his results, our line is slightly convex toward the temperature axis. The values obtained by Magnus appear to differ somewhat more, up to 850°; this is particularly true of his c_p,t-function—which he also assumed to be a linear one—deviating rather strongly toward the temperature axis, as compared with ours, at the higher temperatures. At 600° the divergence between his and White's values and ours already amount to 1 per cent, while at 850° it is about 1.5 per cent. Although these deviations are probably due in part to errors in the temperature measurements—Magnus used iridium-platinum in his furnace and placed the hot junction at the side of, but not within the crucible—this

cannot be the sole cause. This would require errors of between 40 and 75 degrees in the temperature determinations, which cannot be supposed to have been the case; it is more likely that the differences are in some way related to accidental impurities in the metal.

The curve obtained for the specific heat of platinum fits very well with the curve for lower temperatures.[1] We may, therefore, consider the specific heat of platinum to be accurately known now between $-255°$ and $+1625°$, or over a temperature range of almost 1900 degrees.

It is a remarkable fact that up to 1600° there is no indication whatever of a retardation in the increase of the atomic heat under constant pressure, C_p. At 500° C_p equals 6.785 cal., at 1300° it is 7.816 cal., while at 1610° it even amounts to 8.235 cal., and evidently is not approaching a limit. When the specific heat at a constant volume, c_v, is calculated by the general thermodynamic equation already mentioned:

$$c_p - c_v = \frac{0.02345\,(3\alpha)^2 T}{\kappa d}$$

the considerable deviation from the theoretical value still persists. Here 3α is the cubic coëfficient of expansion, T is the temperature, d the specific weight, and κ is the compressibility in kg. per sq. cm.—all quantities being taken at the same value for T. The values of 3α are computed by Holborn's and Day's formula, those for κ are deduced from the data of Bridgman[2] and Grüneisen.[3] The latter has emphasized a probable linear relationship between κ and t. This extrapolation of experimental data to higher temperatures perhaps is not quite permissible; but since in each case κ increases with the temperature, our conclusions will not be changed by possible deviations in this respect, because the true values of κ must lie in such a direction that the difference between c_p and c_v would prove even smaller than is assumed, for the following con-

[1] F. Simon and W. Zeidler, *Z. physik. Chem.*, **123**, 196 (1926).

[2] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 183 (1923).

[3] E. Grüneisen, *Ann. Physik*, (4) **33**, 1264, 1268 (1910). We have used the following values for $10^6\kappa$: at 100° = 0.367; at 500° = 0.401; at 1000° = 0.442; at 1600° = 0.492. The specific gravity of platinum at 15° has been taken as 21.34.

siderations. Bridgman's data for platinum wire, as used by us, are intermediate between Grüneisen's and his own values for bar platinum, being somewhat smaller than Grüneisen's. However, the differences are very small and in all three series of experiments the relation between κ and t seems to be about the same. The data given in Table XXVII for the specific heat at constant volume, c_v, and for the true atomic heat, C_v, of platinum between 100° and 1625° are obtained in this way. The values of c (*sic*) are presented graphically in Figure 129.

This makes it clear that we cannot speak with certainty of c_v approaching a certain limit; moreover it is clear that the value $c_v = 0.03049$, corresponding to $C_v = 3R = 5.963$ cal., is reached below 0°, which clearly indicates that the frequently assumed "emission of electrons" cannot explain why the value 3R is exceeded.[1]

TABLE XXVII

True Specific and Atomic Heats of Platinum at temperatures t° *Centigrade.*

t°	c_v	C_p	C_v
100	0.03142	6.293	6.130
200	0.03202	6.414	6.250
300	0.03256	6.537	6.355
400	0.03306	6.662	6.454
500	0.03353	6.785	6.545
600	0.03386	6.912	6.610
700	0.03421	7.037	6.678
800	0.03448	7.165	6.731
900	0.03476	7.293	6.785
1000	0.03500	7.421	6.831
1100	0.03527	7.552	6.884
1200	0.03550	7.683	6.930
1300	0.03570	7.816	6.969
1400	0.03591	7.949	7.010
1500	0.03610	8.081	7.046
1600	0.03626	8.216	7.079
1700	0.03641	8.353	7.108
1755	0.03651	8.427	7.124

[1] E. Grüneisen, *loc. cit.*; F. Richarz, *Z. anorg. Chem.*, **59**, 156 (1908); A. Einstein, *Ann. Physik*, (4) **22**, 180 (1907); P. Debye, *ibid.*, (4) **39**, 789 (1912); M. Thiessen, *Verhandl. deut. physik. Ges.*, **10**, 950 (1908).

According to another supposition, the abnormally large specific heats in such cases may be connected with some kind of a "heat of transformation" of the metal studied, superimposed upon the amount of heat lost by the hot body. This supposition also fails to stand the test. It will be recalled that, although many of our best investigators have studied platinum with the greatest care, they have never found any indication of an allotropic transformation in the case of this metal. In our calorimeter, however, the heat exchange takes place so rapidly that, even if there were a slow allotropic transformation in this metal, there is no possibility whatever of its superposing any appreciable heat effect upon that due to the cooling of the hot object, within the very brief interval—a few seconds—here involved. It is of interest to remember that such heats of transformation, in the solid state, are usually very small in amount, while in our phenomena we need to account for deviations representing—at higher temperatures—19 per cent and over of the computed values. Even in the highly improbable case that the supposed transformation takes place at such an extreme velocity that it would be completed within the few seconds required for the total heat exchange between the heated object and the calorimeter—a condition in which there would no longer be any real significance in the distinction between a truly "unary" and a "pseudo-unary" system—such great amounts of heat could not possibly have been given off in sufficient excess. In this case and in that of tungsten—where the same phenomenon is repeated—we have, furthermore, heated samples of the pure metals for a long time at a constant temperature and then suddenly quenched them in cold oil or mercury, after which the samples were studied under the X-rays. The spectrograms thus obtained, before and after the heating and quenching, show no changes whatever, either in the intensity or the position of the diffraction lines. For example, the spectrogram (Cu-α-radiation, according to the method of Hull-Debye) of a sample of pure pulverized platinum heated to 1200° for several hours and then quenched in oil at 15°, seemed to

show the same diffraction images with the same relative intensities and the same grating-constant a_0 as a sample not so treated. The same identity between the two spectrograms has been reported for tungsten heated to 700° for several hours and compared with a sample at room temperature. No indication whatever could be found of any change in structure or in density of that metal. For these reasons we think the hypothesis of a "heat of transformation" must be altogether rejected.

The discrepancies between experimental results and theoretical views, here referred to, have been found by previous investigators in a few instances; but the present very accurate determinations up to 1600° now place these facts beyond any doubt and the discrepancies no longer may be ascribed to experimental errors. As Grüneisen first pointed out (*loc. cit*) it seems that there is a constant ratio between the linear coëfficient of expansion, α, and c_p. In the case of platinum this is not true, as is shown by the following values:

Temperature	$\alpha/c_p \cdot 10^6$
0°	285.6
300	276.7
800	270.4
1300	264.7
1600	261.0

Evidently the ratio diminishes rapidly with increasing temperature and this diminution is no apparent linear function of the temperature.

These measurements and others were yet to be extended from the observations between t° and 20° to values between t° and 0°. This made it necessary to extend the measuring methods for c_p to the interval between 20° and 0°, and to do this we had to use a separate calorimeter of simple construction, shown diagrammatically in Figure 130.

A vessel *Zn* is placed in the center of a cylindrical vessel *E* made of enamelled iron and filled with cracked ice. The vessel *Zn* is of sheet zinc, closed by the lid *D* which is also filled with cracked ice. Through this lid passes a

porcelain tube having a stopper *S*, and a stirrer, *r*, and also a calibrated Beckmann thermometer, *Th*, whose scale is divided to 0.001 degree. Inside the vessel *Zn*, and insulated from it by two ebonite supports *f* and *e*, is centered a double-walled sheet-copper vessel *AB*. The wall *A* is polished internally and the wall *B* is polished externally, as perfectly as possible. Within *B* are 200 gm. of water, *W*, in which the stirrer *r* and the thermometer

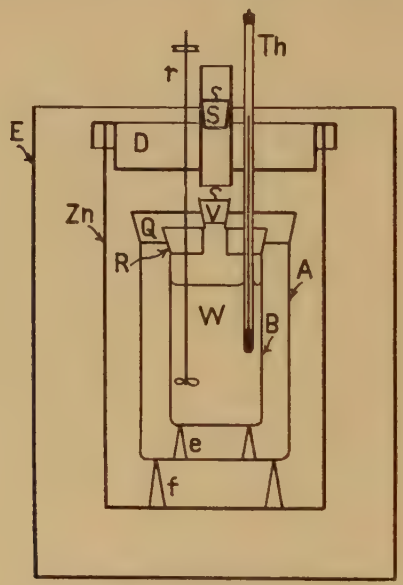


FIG. 130

Th are immersed; any object introduced here loses its heat to the water *W*. *A* and *B* are closed by ebonite covers *Q* and *R* having coaxial central openings whose cylindrical channel can be closed by the hooked stoppers *V* and *S*.

The object to be investigated is heated in a test tube placed in a double-walled water bath of such construction that the whole can be completely inverted at the instant when the object—heated to an accurately determined temperature between 0° and 100°—is dropped into the porcelain tube of the calorimeter, without any loss of heat, so that it enters the water of *B* when the stoppers *S* and *V* are

suddenly removed. The necessary determinations are made in the well-known manner followed when using ordinary liquid-calorimeters. The degree of accuracy attained, although not as high as in the case of the large metallic calorimeter, is evidently sufficient for determining the small correction needed to reduce the measurements to 0° instead of 20°.

The specific heat of pure tungsten we determined in the same way, using the crystallized metal in a perfectly pure state in the form of a thick prismatic bar.

At higher temperatures the determination of the specific heat of tungsten involved many difficulties, chiefly due to the fact that the metal oxidizes very rapidly at temperatures above 600°. The oxidation product formed at lower temperatures is chiefly WO_3, but above 900° this loses oxygen in contact with the metal, and is gradually transformed into a dark indigo blue mixture of oxides, which in turn are transformed at still higher temperatures into a pale green, beautifully crystallized mixture of other oxides of unknown composition. At temperatures above 1300° the latter seems to be so volatile, subliming so rapidly, that so far it has been necessary to stop all measurements at the temperature mentioned. The sublimate thus generated, vehemently and rapidly attacks the hard porcelain protections of the thermocouples and the furnace parts containing silicon and alumina. Therefore, it was impossible to use a porcelain lining in the platinum crucible for heating the metal. Up to 1300°—the highest temperature to which we could carry our measurements on tungsten—platinum fortunately appeared not to be attacked by the heated metal or its oxides; therefore, the protective porcelain lining was omitted in this work. The tungsten was molded into a compact conical mass over 52 gm. in weight and exactly fitting the platinum crucible. This lump was then cut in half on its median plane and a semi-cylindrical excavation hollowed out axially on either half. Through this channel passed the prolongation of the platinum hook from which the crucible was suspended in the furnace. In one of the halves of the tungsten, next to the wall of the crucible, we cut a cylindrical furrow into which fitted

the small thin platinum tube attached to the cover of the crucible and receiving the junction of the thermocouple. In making each measurement, the following data were accurately determined in the following order: (a) the weight of the platinum crucible with its cover, before and after each experiment; (b) the weight of the tungsten before the experiment; (c) the increase in weight of the tungsten due to oxidation, after the experiment; (d) the final weight of the residual tungsten and of the oxides formed during the experiment, first separating them from each other as completely as possible.

The specific heat of WO_3 was also determined at lower temperatures. Soon it became clear, however, that loss of oxygen caused the formation of unknown lower oxides (W_2O_5; W_2O_3?) which, together with WO_3, made up a mixture that was in equilibrium at the respective temperatures, and recognizable by definite colors ranging from pale yellow, through dark indigo blue and yellowish grey, to a dull green. Above 1300° this mixture finally changes into a beautifully crystallized pale greenish, highly volatile mass. The composition of the intermixed oxides and the ratio of the mixture being unknown, in order to correct the observed data it was necessary to determine, in advance, the specific heat of the mixtures of oxides that are obtained by prolonged heating of the tungsten oxide at precisely the same temperatures as those at which the specific heat of the metal was determined, thus making sure that equilibrium actually was established. Since we determined the total quantity of the mixture of oxides formed, every time we made a measurement with the metal, it was possible to apply the small correction we sought as soon as we knew the specific heats of the equilibrium-mixtures of the oxides.

In Table XXVIII we present the results obtained in measuring the specific heats of WO_3 and the yellowish-green mixture of oxides between 500° and 900°; the specific heats, between 1000° and 1300°, of the blue mixture of oxides produced above 925°; finally, the specific heats of the yellowish-green mixture of oxides obtained between 20° and 270°. These last determinations were made by means of

Table XXVIII

Determination of the Mean Specific Heat of the yellowish-green and of the blue Mixtures of Tungsten Oxides between 0° and 1300°C.

A. Yellowish-green mixtures of oxides.

1. Mean specific heat between 2.70° and 20.38°: $\bar{c}_p = 0.0558$.[1]
2. Measurements above 500°C.:

Weight of platinum crucible (g) and of the mixture of oxides (p):	Final temperature of the calorimeter:	Furnace-temperature:	Δt	$\bar{c}_{pt}.m_{pt} + \bar{c}_{ox}.m_{ox}$:	Mean spec. heat $\bar{c}_p$ of the mixture of oxides:
$g = 23.2696$; $p = 8.1810$	20.48	516	0.5063	0.7756+0.6757	0.08259
$g = 23.2696$; $p = 8.1816$	20.73	721	0.7625	0.7907+0.7556	0.09235
$g = 23.2720$; $p = 8.1861$	20.99	908	1.0141	0.8043+0.8192	0.10007

B. Dark blue mixtures of oxides.

$g = 23.1000$; $p = 15.3448$[2]	21.78	1097	1.8024	0.8124+1.5673	0.1021
$g = 23.1070$; $p = 15.3634$	22.16	1292	2.1842	0.8284+1.6140	0.1050

[1] In this experiment we used 12.7052 gm. of the yellowish-green mixtures of oxides in a brass vessel weighing 4.6392 gm.

[2] The crucible contains about twice the weight of oxides mentioned under A, the blue oxides being relatively more dense than the yellowish-green ones.

the calorimeter illustrated in Figure 130. Although incomplete, these data are quite sufficient for our purpose. Calculations show that between 0° and 900° the true specific heat, c_p, of the yellowish-green mixture of oxides at each value of t° can be readily expressed by the formula:

$$c_p = 0.0503755 + 0.13644 \times 10^{-3}t - 0.0490476 \times 10^{-6}t^2.$$

When this formula is applied to the calculation of the mean specific heats of the blue mixture of oxides at 1097°, respectively, the resulting values seem to be considerably larger than the observed values.[1] This means that above 925° other solid phases have appeared in the dark blue mixture, that are characterized by a different relation between specific heat and temperature than that obtaining in the case of the yellowish-green oxides.

The values of Q'_0 are sufficiently represented by the equation:

$$Q'_0 = 0.0274412t + 0.066336 \times 10^{-4}t^2 - 0.030496 \times 10^{-8}t^3 + 0.016953 \times 10^{-11}t^4,$$

and the true specific heat, c_p, of tungsten at each value of t therefore can be calculated from:

$$c_p = 0.0274412 + 0.132672 \times 10^{-4}t - 0.091488t^2 + 0.067812 \times 10^{-11}t^3.$$

Table XXIX gives the values of c_p thus calculated, in its last column. The coefficients of t^2 and t^3 have but slight influence, but at higher temperatures they cause the temperature coefficient of c_p to increase gradually (very slowly).

The values of c_p given in Table XXIX are shown graphically in terms of t by Figure 131. For practical purposes the curve is adequately represented by a straight line and

[1] If the total amount of heat to be accounted for is that given out by the yellowish-green mixture of oxides between 20° and 0°, then the total amounts of heat given out by 1 gm. of the mixture of oxides obtained between t° and 0°, *i.e.* Q_0, are as follows: at 516°, Q_0 = 41.9115 cal.; at 712°, Q_0 = 65.6567 cal.; at 908°, Q_0 = 89.7466 cal.

Experimental results for the blue mixture of oxides give Q_0 = about 111 cal. at 1097°; and 134.5 cal. at 1292°; but if the above equation holds true in its integrated form for the blue mixtures also, then the computed values, 116 and 144 cal., are from 4 to 7 per cent too high.

TABLE XXIX

The Mean and True Specific Heats of Tungsten under Constant Pressure between 0° and 1300°C

A. MEASUREMENTS OF THE SPECIFIC HEAT OF TUNGSTEN BETWEEN 0°C AND 85°C

Used 1.3054 grams of the metal. For the *mean* specific heat $\bar{c}_p$ were found
between 19.45° and 0.42° : $\bar{c}_p = 0.0271$.
between 53.75° and 0.79° : $\bar{c}_p = 0.0276$.
between 83.79° and 0.46° : $\bar{c}_p = 0.0278$.

The *true* specific heat between 0° and 85° can be represented by: $c_p = 0.02659 + 0.0000694t$.

B. MEASUREMENTS BETWEEN 300° AND 1300°C.

Corr. Furnace-temperature °C.:	Final Temperature of the calorimeter:	Δt (observed)	G=Weight of platinum g=Weight of tungsten p = Weight of mixture of oxides	$\bar{c}_{Pt}.m_{Pt} + \bar{c}_W.m_W + \bar{c}_{ox}.m_{ox}$:	Mean specific heat of tungsten $\bar{c}_p$:	Q (cal.) Total amount of heat delivered by 1 gm. tungsten between t° and 20°:	Q_0(cal.) Total Amount of heat delivered by 1 gm. tungsten between t° and 0°:	Q'_0(cal.) Values of Q_0 from formula:	True specific heat c_p of tungsten at t°:	
									t°	c_p
306.7	20.48	0.4656	G=23.292 g=52.249	0.7609+1.5492=2.3101	0.02958	8.4664	9.0327	9.0324		
									100	0.02876
408	20.59	0.6408	G=23.292 g=52.249	0.7684+1.5804=2.3488	0.03025	11.7192	12.2885	12.2837	200	0.03006
									300	0.03136
505	20.71	0.8144	G=23.292 g=52.249	0.7756+1.6125=2.3881	0.03086	14.9452	15.5179	15.5099	400	0.03264
									500	0.03393
602	20.95	0.9926	G=23.270 g=52.251	0.7819+1.6439=2.4258	0.03146	18.2800	18.8593	18.8796	600	0.03522
									700	0.03651
721	21.16	1.2222	G=23.265 g=51.516 p= 0.342	0.7906+1.6576+0.0316 =2.4798	0.03218	22.5211	23.1062	23.1650	800	0.03782
									900	0.03914
909	21.54	1.5866	G=23.268 g=49.898 p= 0.659	0.8044+1.6685+0.0659 =2.5388	0.03347	29.7036	30.2992	30.3113	1000	0.04047
									1100	0.04183
1097	22.06	1.1094	G=23.281 g=51.399 p= 1.827	0.8188+1.7808+0.1866 =2.7862	0.03469	37.2891	37.8991	37.9286	1200	0.04322
									1300	0.04463
1292	22.80	2.4132	G=23.312 g=47.196 p= 1.630	0.8357+1.6918+0.1714 =2.6989	0.03587	45.5259	46.1563	46.3411		

c_p is sufficiently expressed by the linear function $c_p = 0.02744 + 0.00001132t$. The true curve is but slightly concave upwards.

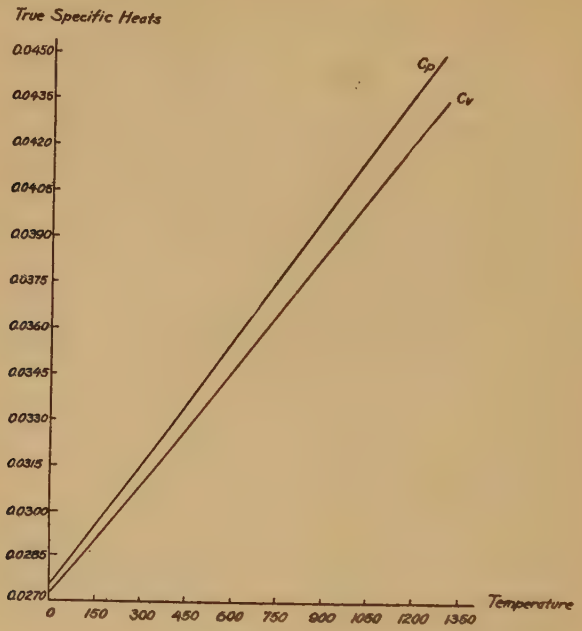


FIG. 131

The values of c_p here determined depart very markedly from those previously obtained by other investigators using indirect methods, and particularly from values determined by means of evacuated incandescent electric bulbs.[1] A method proposed originally by Corbino, and subsequently improved by Worthing and Gaehr, and also applied with some variation by Smith and Bigler and Bocksthaler, makes use of observed changes in radiation, electrical resistance, and temperature of a thin tungsten wire, as related to the time elapsed since the instant when the current intensity in the wire is suddenly changed. Although this method is ingeniously devised it does not

[1] M. von Pirani, *Verhandl. deut. Physik. Ges.*, **14**, 375 (1912); O. M. Corbino, *Physik. Z.*, **13**, 375 (1912); A. G. Worthing, *Phys. Rev.*, (2) **12**, 199 (1918); P. F. Gaehr, *ibid.*, (2) **12**, 396 (1918); K. K. Smith and P. W. Bigler, *ibid.*, **19**, 268 (1922); L. I. Bocksthaler, *ibid.*, **25**, 677 (1925).

impress one as permitting exact, reproducible determinations of c_p. In the equations that apply to this experiment, c_p enters as one of several factors in a single term which expresses a considerable percentage of the total observed effect. The method is very complicated and there are many sources of error. The lack of agreement among the data obtained by different observers, and even by the same observer at different temperatures; also the mysterious discrepancies that occur in those cases when the wire is either heated or cooled; and the necessity for determining the temperature of the wire at any moment by means of an optical pyrometer, are some of the numerous circumstances that arouse serious doubts concerning the reliability of the method and of the results obtained by it. In contrast to this, our direct and thoroughly perfected determinations of the specific heat exclude, beforehand, any considerable experimental errors, so that the latter may be regarded as of secondary significance when seeking an explanation of the differences mentioned above. Moreover the oxidation of the compact, crystallized metal plays an insignificant rôle at temperatures up to 721° so that the correction for it is negligible even at this temperature. Our results between 0° and 20°, obtained by direct measurement, are in full agreement with the best data given in the literature; and the values for temperatures above 721° are as conformable with those for c_p below 721° as can be desired. For these reasons we are convinced that the observational data presented here from our direct measurements are much more reliable than those secured by the indirect methods described above.

On the other hand, Magnus and Danz have recently published[1] the results of a number of measurements—also direct measurements—of the specific heat of tungsten between 400° and 900°, that are in complete disagreement with ours. It is true, they also find a linear relationship between c_p and t; but the straight line graphically representing their results is much less steep than ours, although their values are much larger. The straight line of these German investigators is therefore located, throughout its

[1] A. Magnus and H. Danz, *Ann. Physik*, 81, 407 (1926).

whole extent, far above our line as shown in Figure 131. At 600° their value for c_p is 13 per cent, and at 100° not less than 30 per cent greater than our values; moreover they calculate, by extrapolation, a value for c_p (at 0°) = 0.03685 which is about 34 per cent higher than our actually measured value at that temperature—our value being in close agreement with that found by other observers, as has been remarked. In connection with the data by Magnus and Danz, we find abnormally high values for the atomic heat, C_p, *e.g.* at 0° it would be 6.78 and at 900° it would even reach 7.7.

In our opinion, this apparent incompatability of results and the abnormal values for C_p are easily understood if one bears in mind the above described difficulties encountered in making such measurements. In the first place, they may have been influenced by inaccurate temperature indications due to using iridium-containing platinum in the furnace. Of much more importance, however, is the fact that in their experiments Magnus and Danz repeatedly employed heated tungsten powders. Early in the course of our own experiments it became clear to us that the metal in the powdered form is absolutely unsuited to this kind of measurement. On heating equal weights of tungsten in the powdered form and as a compact, crystallized, metallic bar, it was found that at 1000° the powder was completely converted into an oxidation product within 15 minutes, while the metal in bar form was thinly coated, on its outer surface only, with oxides. Moreover, prolonged heating of the metal in the powdered form, at even so low a temperature as 300°, resulted in the oxidation of the greater portion of the powder; the compact bar, being of the nature of a single crystal, was not attacked at all under these conditions. Therefore, by using the metal in the powdered forms Magnus and Danz must have been experimenting with a preparation which, even after the first heating at 600°, consisted in large part of a mixture of oxides. In their subsequent experiments this material must have been converted completely into those oxide-mixtures that are in equilibrium with the metal at the same corresponding temperatures. In their measurements, there-

fore, it is probable that there was no longer any metallic tungsten present; thus not only was the ratio W:W-oxide altered during their experiments, as they supposed, but the degree of oxidation of the mixture was changed also.

That we here have to do with not only a single oxide, WO_3, but with a complete mixture of several oxides, the composition depending on the particular circumstances during the heating, has been fully demonstrated by us in a series of experiments. If the quantity of oxide formed is computed from the amount of oxygen taken up by the sample, on the wrong assumption that WO_3 only was formed, the results obtained at 600° appear to be quite erroneous. It was because of these very experiences with the true nature of these oxidation processes, that we finally proceeded to determine separately the specific heats of the equilibrium mixtures of these oxides; and to measure not only the amount of oxygen taken up, but also the weight of the remaining metal and of the mixture formed, thus obtaining the necessary corrections for our observed values. The high values obtained by the German observers are fully explained by the simple fact that, for each temperature, the specific heats of these oxide mixtures are much higher than those of the tungsten itself. This also makes clear why their c_p,t-curve—extrapolated to lower temperatures from wrong values observed at higher ones—must be located altogether above the normal straight line; their observed values do not relate to the metal itself but to the mixture of oxides with their much higher specific heats or to the oxides plus a remnant of the metal which coexists at the same temperature. Evidently such an extrapolation to lower temperatures must give much too high values, so that the resulting straight line would have a less steep inclination toward the t-axis than the line obtained by our direct measurements. The value of c_p for 0°, as published by the same authors, also departs from the value found by direct measurement at that temperature.

When we consider the above relationship between temperature and specific heat of tungsten, there appears to be no indication of a possible allotropic transformation

of the metal between 100° and 1300°. The behavior of tungsten under elastic and tensile strains, led certain American investigators, in the laboratory of the General Electric Company[1] in Schenectady, to assume the presence of a kind of transformation point at about 560° and another at 1375°, where the metal seemed to show certain discontinuities in its tensile strength, etc., considered as a function of the temperature. Concerning these experiments, it is still quite doubtful whether the mechanical properties of the metal, under these circumstances, should be ascribed to a mere change in mutual orientation of the microscopic crystalline individuals under the influence of the applied external forces, or whether real "allotropic transformations"—in the sense of heterogeneous equilibria—are occurring here. The American authors try to support their views by a special interpretation of their measurements on the thermal expansion of the metal. It is true, the numerical results are in perfect agreement with those previously obtained by Worthing[2] and expressed by him, between 300° Abs. and T° Abs., by the formula:

$$L_T = L_{300}\{1 + 4.44 \times 10^{-6}(T-300) + 4.50 \times 10^{-11}(T-300)^2 + 2.2 \times 10^{-13}(T-300)^3\},$$

where L is the length of the tungsten bar at T° Abs. and L_{300} is the length at 300° Abs.

We may therefore represent the relation of the linear thermal coëfficient of expansion, α, to t°C. by the expression:

$$\alpha \times 10^6 = 4.4402 + 0.09034 \times 10^{-3}t + 0.633 \times 10^{-6}t^2.$$

The American workers divide this curve into three separate parts, each of which shows a linear relation between α and t, viz.: between 100° and 577°C, α, $= 4.50 \times 10^{-6}$; between 577° and 1377°C, $\alpha \times 10^6 = 5.20$ to 5.70; above 1377° (up to 2220°C), $\alpha = 7.27 \times 10^{-6}$. Evidently it is quite questionable whether there is any real significance in such a division of a curve into rectilinear parts; and whether this has not been done with the sole purpose

[1] *Phil. Mag.*, 48, 245 f. (1924).

[2] A. G. Worthing, *Phys. Rev.*, (2) 10, 638 (1917).

of furnishing apparently stronger support to the premise that the results of the measurements of the tensile strength, as a function of temperature, must parallel an analogous localization of discontinuities in the temperature-functions of other properties of that metal. The authors' exposition is not sufficient or suitable to convince one of the correctness of the view proposed.

In any case, it is certain that our results on the specific heat of tungsten, and its essentially linear dependence on temperature, bring up no question of any discontinuity at 550° or 570°. We did not continue our experiments above 1300° for the reasons already mentioned, therefore we cannot yet decide with certainty as to the presence or absence of a transition temperature above 1375°C. The Roentgenographic study of the heated tungsten, as described above, fully proves that no allotropic transformation occurs between 560° and 700°C.

We have calculated the values of c_v at each temperature from the corresponding values of c_p, using the same general relations that were employed in the case of platinum. For calculating the cubic coefficient of expansion of tungsten we use Worthing's formula for the linear expansion, because his formula gives values identical with the measurements obtained in the Laboratory of the General Electric Company as mentioned above. Bridgman has measured the compressibility, but for two temperatures only, 30° and 75°.[1] According to Grüneisen's reasoning, it is highly improbable that there should be any appreciable deviations from linearity; moreover, the temperature coefficient of κ is very small and since the thermal expansion is also very small, the whole correction-term for $(c_p - c_v)$ in the case of tungsten is very small. The fundamentally unpermissible extrapolation of the supposed linear κ,t-function can cause but insignificant errors and the true value of c_v is surely but slightly larger than those here employed, so that $(c_p - c_v)$ would be yet smaller than the values here found for it.

Taking account of the foregoing considerations, and adopting 19.137 as the specific weight of bar tungsten at

[1] Bridgman, *Proc. Am. Acad. Arts Sci.*, 58, 182 (1923).

15°, we have calculated the values of c_v with the corresponding atomic heats, Ac_v, from our determinations of c_p for a series of temperatures between 100° and 1300°. The atomic heat and c_v as thus computed are presented in Table XXX. Figure 131 presents in graphic form c_v and c_p as functions of temperature, and the practically straight-line character of both curves is evident.

These data make it clear that—as in the case of platinum—the maximum value of $3R = 5.963$ cal. is attained at a relatively low temperature (about 400°), and gradually increases to about 8.0 cal. at 1300°. Since c_v varies with t practically as a straight line, there is no indication that it gradually approaches a limiting value at higher temperatures, and it is apparent that probably no such limiting value exists.

TABLE XXX

Values of the True Specific Heat c_v of Tungsten at Constant Volume and of the Atomic Heat, Ac_v, at Temperatures between 0° and 1300°

Temperature	c_v cal.	C_v cal.
0°	0.02730	5.023
100	0.02847	5.239
200	0.02976	5.476
300	0.03098	5.700
400	0.03229	5.941
500	0.03355	6.173
600	0.03475	6.394
700	0.03601	6.625
800	0.03724	6.853
900	0.03850	7.084
1000	0.03958	7.283
1100	0.04066	7.482
1200	0.04162	7.658
1300	0.04347	7.998

In the same way we made preliminary determinations of the specific heats of pure rhodium and pure palladium—using the platinum crucible already mentioned. The samples of these metals were perfectly pure, being lent us by the firm of Heraeus. Originally the metals were used in the

powdered form; but it was found that at high temperatures these powdered metals took up hydrogen, they were therefore melted into small spheres, whereby we seem to have completely removed this objection.

In the case of rhodium we used the water calorimeter to determine its specific heat between 1.7° and 73°, obtaining the value 0.0593; and between 20.1° and 72° we found 0.0598. It follows from these determinations, allowing for an uncertainty of about 0.6 per cent, that the total amount of heat given off between 20° and 0° by 1 gm. of this metal averages 1.1572 calories. All the data we obtained are summarized in the usual way in Table XXXI. These values (and the same is true for the corresponding ones for palladium in Table XXXV) are offered with considerable reservations as to their accuracy; they must be rechecked before finally accepting them. The symbol A in Table XXXI indicates the sum $(\bar{c}_{Pt}m_{Pt} + \bar{c}_{Rh}m_{Rh})$ where $\bar{c}_{Pt}$ is the mean specific heat of platinum within the temperature interval considered, and m_{Pt} and m_{Rh} are the weights of the respective metals present during the observation. The mean specific heat of rhodium is then found from A thus:

$$\bar{c}_{Rh} = \frac{A - \bar{c}_{Pt}m_{Pt}}{m_{Rh}}$$

The total amount of heat, in calories, delivered by 1 gm. of rhodium between t° and 0° can be calculated by the equation:

$$Q_0 = 0.054994 + 3.12264 \times 10^{-5}t^2 - 7.8056 \times 10^{-9}t^3.$$

so that the true specific heat at each temperature can be found from the formula:

$$c_p = 0.054994 + 6.2453 \times 10^{-5}t - 2.3417 \times 10^{-8}t^2.$$

At 0°, c_p = 0.05499, at 100° = 0.06100, at 200° = 0.06655, at 300° = 0.07162, at 400° = 0.07623, at 1600° = 0.09497(extr.), at 1700° = 0.09349(extr.). These and other values are presented graphically in Figure 132 (p. 393).

The remarkable feature of the curve for rhodium, Fig. 132, is the maximum, *M*, in the neighborhood of 1350°; the value of c_p at 1600° being about the same as at 1050°,

TABLE XXXI

Mean and True Specific Heats, under constant Pressure, of Rhodium between 0° and 1500°.

Temp. (corr.)	Final Temp. of Calorimeter	Δt (obs.)	Weight of Rhodium	Weight of Platinum	$A = c_{Pt}m_{Pt} + \bar{c}_{Rh}m_{Rh}$ between t and t′	Mean spec. heat of Rhodium $\bar{c}_{Rh}$ between t and t′	Total amount of heat Q delivered by 1 gm. Rh between t and t′	Total amount of heat Q_0 delivered by 1 gr. Rh between t and 0°	True specific heat c_p of Rhodium at t°	Atomic Heat of Rhodium C_p at t°
t°	t′		gm.	gm.						
503.0	20.88	0.8675	28.118	22.396	2.68962	0.06914	33.333	34.575	0.08048	8.281
600.5	21.08	1.0695	28.118	22.397	2.75912	0.07136	41.348	42.602	0.08404	8.648
714.6	21.30	1.3189	28.118	22.397	2.84340	0.07408	51.357	52.627	0.08768	9.022
802.9	21.49	1.5131	28.118	22.387	2.89442	0.07568	59.137	60.415	0.09004	9.265
1039.9	22.06	2.0552	28.118	22.404	3.01820	0.07947	80.886	82.198	0.09486	9.761
1107.2	22.16	2.2137	28.118	22.404	3.04972	0.08040	87.238	88.556	0.09543	9.820
1313.2	22.60	2.7042	28.118	22.391	3.13210	0.08280	106.863	108.211	0.09662	9.943
1400.2	22.89	2.9165	28.118	22.395	3.16520	0.08384	115.470	116.831	0.09653	9.933
1500	23.16	3.1602	28.118	22.380	3.19854	0.08466	125.026	126.403	0.09598	9.877

The true specific heat, c_p, at t° between 500° and 1500° may be calculated from the formula:

$$c_p = 0.054994 + 6.2453 \times 10^{-5}t - 2.3417 \times 10^{-8}\,t^2.$$

and that at 1700° about the same as that at 960°. In this case it may be suspected that a secondary heat effect is superimposed upon the normal one, due perhaps to an allotropic change in the metal. In an effort to settle this doubt, we heated the metal continuously at 1500°, then suddenly quenched it by dropping into cold mercury, the sample having been wrapped in thin platinum foil before heating. After quenching, a powder spectrogram was made with Cu-α-radiation, and the diffraction image obtained was compared carefully with one made from a sample of rhodium prepared by reducing a rhodium salt and not previously heated. Both radiograms appeared perfectly identical, corresponding to the face-centered cubic grating of ordinary rhodium obtained with $a_0 = 3.79$Å, and having a calculated density of 12.2.[1] The only observable difference between the two radiograms was that in the radiogram from the heated sample the lines were much sharper, due to better crystallization, than in that for the other sample. We found no indication whatever of an allotropic change in this case. The observation must, therefore, record a real fact. This is the first observed instance where a homogeneous pure metal shows a decrease in its specific heat under constant pressure, c_p, at rather high temperatures that are far below its melting point. However, as has just been stated, these data need further checking before they can merit final acceptance.

The computed atomic heats, C_p, have been collected in Table XXXII. Just as in the case of platinum, the value 6.4 is passed at a relatively low temperature (about 125°C.) and the atomic heat increases rapidly to about 9.95 cal. at 1360°. Its values remain far above 9 calories at higher temperatures also. Here is a further illustration of the fact that modern theories of specific heat are insufficient; because the atomic heat at constant volume, C_v, cannot differ from C_p to such an extent as ever to reduce these values to the theoretical figure of 5.956 calories.

Although no exact measurements of the cubic coëfficient of expansion, 3α, and of the compressibility, κ,

[1] A. W. Hull, *Phys. Rev.*, 17, 571 (1921); V. M. Goldschmidt, Barth and Lunde, *Skrifter Norske Videnskaps-Akad. Oslo, I. Matemat.-Naturv. Klasse*, 1, No. 7 (1925).

TABLE XXXII

Atomic Heats of Rhodium, C_p, *under constant Pressure*

Temperature °C	C_p calories
0	5.659
100	6.277
200	6.848
300	7.370
400	7.844
503	8.281
600	8.648
715	9.022
803	9.265
1040	9.761
1107	9.820
1313	9.943
1400	9.933
1500	9.877
1600	9.773
1700	9.620

at higher temperatures, are available,[1] it is possible to estimate the values of C_v. Considering the most probable values, so that the difference $(C_p - C_v)$ has too large rather than too small values, we may calculate the approximate values of c_v and C_v given in Table XXXIII

While no accuracy may be claimed for these figures they cannot be far from the true ones; and at any rate, they give a vivid idea of the fact already mentioned, viz., there can be no doubt at all that the corrections to be applied to C_p are far too small to bring the high values of C_p down to the theoretical value of C_v. The theoretical limit in this case appears to be exceeded before 100° is reached.

[1] The linear coefficient of expansion, α, was measured by S. Valentiner and J. Wallot, *Ann. Physik*, 46, 837 (1915). They found between 6° and 21°, $\alpha = 0.00000876$. In 1869 H. Fizeau, *Compt. rend.*, 68, 1175 (1869), found 0.00000858 at 50°. For the compressibility κ I have adopted the value 0.5×10^{-6} in kgm./sq. cm., which cannot be far from the correct one. The density d was taken as 12.2 at 0°.

TABLE XXXIII

Approximate Values of c_v and C_v for Rhodium at different Temperatures

°C	c_v	Atomic Heat C_v
0	0.05427	5.584
100	0.06001	6.175
200	0.06529	6.718
300	0.07009	7.212
400	0.07342	7.555
503	0.07839	8.066
600	0.08168	8.405
715	0.08500	8.746
803	0.08712	8.965
1040	0.09126	9.390
1107	0.09165	9.430
1313	0.09224	9.491
1400	0.09190	9.457
1500	0.09106	9.370
1600	0.08976	9.237
1700	0.08799	9.054

The measurements on palladium (M.pt. = 1549.2°C.) were made in the same way. Up to the present they have been carried out up to about 1300°. In the case of this metal the insufficiency of the theory will be seen to be yet more convincingly proved.

Perfectly pure palladium was employed, the platinum crucible being filled with more than 25 gm. of the metal previously melted and resolidified in small droplets. The data have been collected in Table XXXIV.

From the total amount of heat, Q, delivered between 398.5° and 0°, between 810.7° and 0°, and between 1094.8° and 0°, we deduced the following equation for Q, and find it to serve quite satisfactorily for the amounts of heat observed to be delivered between other temperatures and 0°:

$$Q = 0.058579t + 0.000028082t^2 - 0.000000001916 1t^3$$

Therefore, the specific heat, C_p, at each temperature, t, is given by the equation:

$$C_p = dQ/dt = 0.058579 + 0.00005616 4t + 0.000000005748 3t^2,$$

TABLE XXXIV

Mean and True Specific Heats, under constant Pressure, of Palladium between 0° and 1200°C.

Temperature t in °C. (corr.)	Final Temp. of Calorimeter t′	Increase of Temperature of Calorimeter: Δt	Weight of Palladium	Weight of Platinum	$\bar{c}_{Pt}m_{Pt}+\bar{c}_{Pd}m_{Pd}$	Mean spec. heat $\bar{c}_{Pd}$ of Pd between t and t′	Total Heat delivered between t′ and 0°C.	between t and t′	between t and 0°	Amount of Heat Q'_0 as calculated from formula
			gm.	gm.			(cal.)	(cal.)	(cal.)	(cal.)
398.5	20.65	0.66330	25.070	22.395	2.4938	0.07003	1.220	26.462	27.682	—
521.0	20.90	0.90908	25.070	22.396	2.5763	0.07293	1.235	36.498	37.733	37.872
642.4	21.15	1.1641	25.070	22.402	2.6618	0.07604	1.250	47.238	48.488	48.846
810.7	21.54	1.5495	25.070	22.395	2.7893	0.08066	1.273	63.653	64.926	—
935.7	21.83	1.8478	25.070	22.396	2.8723	0.08354	1.290	76.345	77.635	78.240
1094.8	22.24	2.2515	25.070	22.397	2.9820	0.08710	1.314	93.960	95.274	—

The mean specific heat of palladium between 0° and 80°C was determined as 0.06135; that between 20° and 80°C as 0.06210.

an equation that permits one to calculate the true specific heat, C_p, of palladium with sufficient accuracy.

The determinations for temperatures between 80° and 0°, and between 20° and 0° were made by means of the water calorimeter described. The values of C_p for palladium are represented graphically in Figure 132.

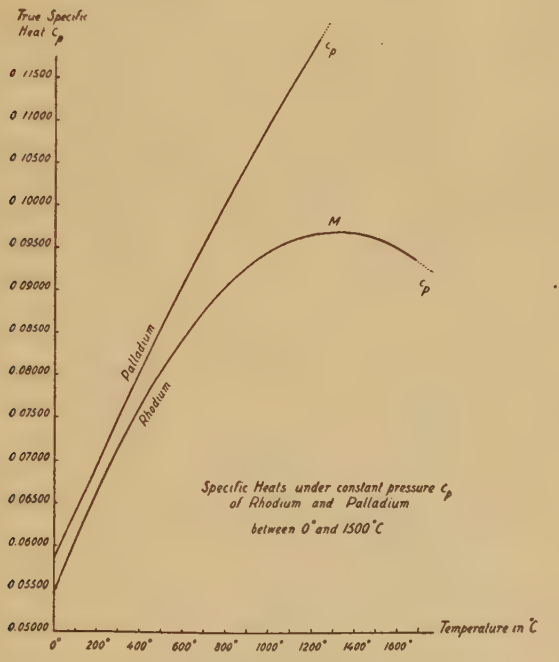


FIG. 132

The values for c_p and C_p, at constant pressures, have been calculated for several temperatures, and are presented in Table XXXIV. The curve for c_p (Fig. 132), which deviates but slightly from a straight line, also has been extrapolated for a few hundred degrees, but all these temperatures are below the melting point of palladium. The approximate values, C_v, have been calculated by the general thermodynamic expression previously mentioned. In order to compute the coëfficient of cubic thermal expansion, 3α, required for this formula, we have resorted

to Holborn's and Day's relation for the linear thermal expansion of palladium between 0° and 1000°, viz.,[1]

$$l_t = l_0(1 + 0.00001167t + 0.0000000021 87t^2).$$

Not knowing the compressibility, κ, of the metal, we were obliged to make what we consider a rather probable estimate of its value, with reference to the corresponding values for the other metals of this group. We adopted for κ the value 0.6×10^{-6} kg./sq. cm. The specific gravity of palladium at 0° = 11.92; its atomic weight is 106.7

The approximate values of c_v and of the atomic heat, C_v, at constant volume as thus calculated, are also presented in Table XXXV for the sake of comparison.

The data in Table XXXV need confirmation[2] by further experiment before they are to be accepted as accurate; but even as they stand, they furnish a very striking proof of the insufficiency of the modern theories of the specific heat. Even at a temperature as low as 100°C. the value 6.4 for C_p, as derived from Dulong's and Petit's empirical rule, appears to have been already exceeded, and at higher temperatures increases to more than double that value. As in all the cases hitherto considered, the corrections that are to be applied to c_v are quite inadequate to reduce the observed values of c_p to figures that are of the magnitudes called for by the Einstein and Debÿe theory. Even for C_v the values seem to exceed the theoretical limit of 5.976 cal. by more than that amount itself. The conclusion seems justified, indeed, that this behavior on the part of refractory metals is a general one; and it is hardly possible to continue to doubt the inadequateness of the assumption of such a maximum limit at high temperatures as the quantum theory requires.

In all the cases considered, viz., platinum, tungsten, rhodium and palladium, there seems to be no limiting maximum value for C_p in the vicinity of 6.4 cal. (Dulong and Petit), or of $3R = 5.956$ cal. for c_v. Already at temperatures far below the melting point, C_v exceeds this

[1] L. Holborn and A. L. Day, *Ann. Physik*, (4) **2**, 505 (1900).

[2] Later it appeared that in the case of palladium the wires of the thermocouple had been contaminated. Those temperatures therefore need careful redetermination.

TABLE XXXV

The true Specific Heats c_p of Palladium under Constant Pressure at different Temperatures at the corresponding Atomic Heats C_p; also the approximate values c_v and C_v at Constant Volume.

°C.	True Specific Heat c_p	True Atomic Heat C_p	Approximate Values of c_v	Approximate Values of C_v
0	0.05858	6.250	0.05719	6.102
100	0.06414	6.844	0.06229	6.646
200	0.06958	7.424	0.06728	7.179
300	0.07491	7.993	0.07217	7.701
398.5	0.08004	—	—	—
400	0.08012	8.549	0.07686	8.201
500	0.08522	9.093	0.08139	8.684
521	0.08628	—	—	—
600	0.09021	9.625	0.08575	9.149
642.4	0.09229	—	—	—
700	0.09508	10.145	0.09001	9.603
800	0.09983	10.652	0.09404	10.034
810.7	0.10033	—	—	—
900	0.10477	11.147	0.09796	10.452
935.7	0.10610	—	—	—
1000	0.10899	11.629	0.10167	10.848
1094.8	0.11318	—	—	—
1100	0.11340	12.100	0.10524	11.229
1200	0.11770	12.559	0.10867	11.596
1300	0.12210	13.028	0.11218	11.970
1400	0.12594	13.438	0.11512	12.284
1500	0.12989	13.860	0.11794	12.584

value of 3R in some cases, and in all cases C_p attains values far above those to be expected, especially if one considers the magnitudes of 3α and κ for calculating C_v.

It seems to be fairly certain, therefore, that the modern formulation of the theory of specific heat may not yet be regarded as a final one. Evidently C_v has no such limit as 3R calories.

Born and Brody[1] have tried to extend the considerations of the theory of quanta leading to these theories of spe-

[1] M. Born and E. Brody, *Z. Physik*, 6, 136 (1921); M. Born, *Enzyklop. math. Wiss.*, v. V-3, 698.

cific heat, in such a manner as to make this limiting condition unnecessary. By taking into account the non-harmonic character of the oscillations at high temperature, where the amplitudes of the oscillating bodies become rather large, they are able to derive an equation for C_v having the form: $C_v = 3R(1 - 6\sigma RT)$, where σ can ordinarily be negative—according to them—so that C_v might possibly exceed the value of 3R. The factor $\sigma = (\sigma' + \sigma'')$, where σ' is always less than zero and σ'' is greater than zero, their sum being negative if the absolute value of σ' is greater than that of σ''. But σ' is connected with the 3d-order terms for the potential energy, and σ'' with the 4th-order terms, the factors represented by σ' allowing particularly for the thermal expansion of the substance. From these considerations one must conclude that such a linear increase of C_v and t above the value 3R would take place chiefly in substances having considerable thermal expansion.

Our experiments teach us just the opposite to the above. Take the case of platinum in particular, with its very small expansion coëfficient, and even more so the case of tungsten having a yet smaller coëfficient of expansion; exactly here we found the greater deviations. The extension of the theory mentioned, therefore cannot yet satisfactorily account for the true behavior of these substances at higher temperatures, these phenomena being now established beyond all doubt.[1]

Therefore, if it should appear that these phenomena are generally observed, it will be inevitably necessary to so modify the present fundamental conceptions of the theory that its limiting condition may be eliminated; in that case, however, it will no longer be possible to offer a rational explanation of Dulong's and Petit's well-known empirical rule for higher temperatures.

In conclusion, as a further illustration of the sensitiveness of our calorimetric method as an indicator of some kind of reaction taking place in the solid under in-

[1] In a recent paper in *Naturwissenschaften*, 15, 825 (1927), A. Sommerfeld points out that at high temperatures the electronic motion of the metal probably can contribute not more than about 1/100 R to the increase of C_v above the supposed maximum value.

vestigation, we shall discuss the phenomena observed by us in the case of two kinds of refractory porcelains, which we expected to use as linings for our platinum crucibles when the latter seemed to be in danger of attack by the metals studied.

We had at our disposal porcelain crucibles provided with screw covers and of such dimensions that they exactly fitted the platinum crucibles we were using. The two kinds of porcelain may be designated I and II. Chemical analysis shows that both porcelains were essentially an aluminum silicate with admixtures of small amounts of potassium, magnesium and iron silicates. Their percentage compositions were:

Porcelain I		*Porcelain II*	
SiO_2	65.14%	SiO_2	41.1%
Al_2O_3	28.76	Al_2O_3	57.1
Fe_2O_3	1.08	Fe_2O_3	0.3
K_2O	3.61	CaO	traces
MgO	1.21	MgO	0.5

Porcelain II appeared to be refractory even at the highest temperatures attained, but Porcelain I softened at 1100–1300° and was no longer usable at 1600°C. The values obtained in the course of the determination of the specific heats of these two porcelains are presented in Table XXXVI.

The specific heat c_p of Porcelain I can be calculated by the equation:

$$c_p = 0.17510 + 2.2284 \times 10^{-4}t - 0.77124 \times 10^{-7}t^2$$

with great accuracy.

The specific heat of Porcelain II is very accurately represented by the equation:

$$c_p = 0.20698 + 1.1231 \times 10^{-4}t - 0.5685 \times 10^{-8}t^2.$$

When the results for these two porcelains are plotted graphically (Fig. 133) the differences in the behavior of the two is at once clear. While the curve for Porcelain II is quite normal, that for the less refractory Porcelain I begins to bend toward the t-axis at temperatures as low as 800° or 900°; the curve is almost parallel with Porce-

TABLE XXXVI

Specific Heats of Porcelains

Temperature °C. corr.	Final temperature t′ of the calorimeter	Rise of temp.	Weights of porcelain (=s): and of platinum (=p)	Total amount of heat delivered between t° and o° cal.	Amount of heat delivered by p gram of platinum cal.	Total amount of heat del. by 1 gm. porcelain between t° and t′	Total amount of heat del. by 1 gm. porcelain between t and o°.	Total amount of heat calculated: from the formula:	True specific heat of porcelain at t°.
PORCELAIN I BETWEEN o° AND 1536°									
405.8	20.70	0.68286	s= 8.0182 p=23.4526	969.66	997.18	83.868	87.663	87.686	0.2528
504.7	20.92	0.8803	s= 8.0182 p=23.4206	1252.9	377.42	109.19	112.88	113.44	0.2679
604.5	21.19	1.0938	s= 8.0182 p=23.4201	1553.1	458.66	136.49	140.38	140.89	0.2816
730.85	21.43	1.3752	s= 8.0182 p=23.4292	1952.7	564.79	173.09	177.02	177.45	0.2968
853.2	21.67	1.6597	s= 8.0182 p=23.4298	2355.7	669.67	210.28	214.25	214.54	0.3091
952.1	21.67	1.8952	s= 8.0182 p=23.4400	2691.2	756.58	241.28	245.25	245.52	0.3174
1064	22.09	2.1680	s= 8.0182 p=23.4239	3078.6	855.78	277.22	281.27	281.47	0.3249
1206.4	22.54	2.5278	s= 8.0182 p=23.4478	3589.6	986.08	324.70	328.83	328.25	0.3317
1289.7	22.69	2.7393	s= 8.0182 p=23.4308	3889.8	1062.8	352.57	356.73	356.00	0.3342

TABLE XXXVI (Continued)
Specific Heats of Porcelains

Temperature °C corr.	Final temperature t′ of the calorimeter	Rise of temp.	Weights of porcelain (=s) and of platinum (=p)	Total amount of heat delivered between t° and o° cal.	Amount of heat delivered by p gram of platinum cal.	Total amount of heat del. by 1 gm. porcelain between t° and t′	Total amount of heat del. by 1 gm. formula: between t and o°.	Total amount of heat calculated: from the formula:	True specific heat of porcelain at t°.
1411.8	23.04	3.0487	s= 8.0182 p=23.4308	4329.2	1177.9	393.02	397.25	396.92	0.3360
1535.5	32.36	3.3595	s= 8.0182 p=23.4462	4770.4	1298.0	433.06	437.34	438.47	0.3355
			PORCELAIN II BETWEEN 0° AND 1600°						
395.0	20.78	0.78523	s= 9.7082 p=22.716	1115.1	279.77	86.044	90.406	90.403	0.2510
520.3	21.03	1.0741	s= 9.7082 p=22.715	1525.2	377.72	118.48	122.60	122.62	0.2649
701	21.51	1.5132	s= 9.7082 p=22.714	2148.8	522.96	167.47	171.99	172.03	0.2848
887.7	21.99	1.9959	s= 9.7082 p=22.723	2834.1	678.39	222.05	226.67	226.67	0.3052
1097.3	22.56	2.5659	s= 9.7082 p=22.722	3643.7	858.84	286.86	291.60	292.24	0.3279
1293.1	23.14	3.1389	s= 9.7082 p=22.723	4457.2	1033.4	352.67	357.53	357.44	0.3490
1591	24.06	4.0590	s= 9.2082 p=22.720	5763.9	1310.1	458.77	463.82	463.82	0.3809

lain II at 1200°, passes through a maximum at about 1400° and begins to descend in the vicinity of 1550°. There can be no doubt whatever, that all this divergent behavior in this specimen is due to sintering; evidently this begins slowly at temperatures even below 800° or 900°, and goes

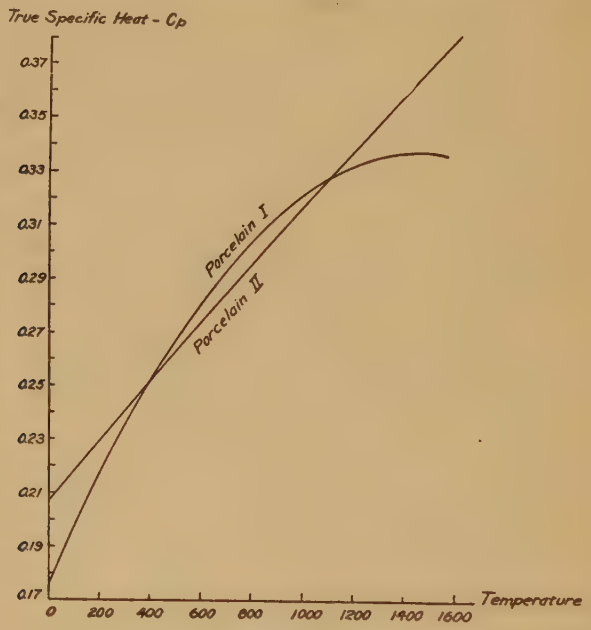


FIG. 133

on with increasing speed as the chemical reactions between its different components set in at ever increasing rate, while the softening of the porcelain indicates an incipient fusion that is causing heat to be absorbed. Melting seems to be almost complete at 1500° to 1550°, the value of c_p being slightly smaller at 1536° than at 1412°.

CONCLUSION

In the preceding lectures I have tried to give you some idea of the very great difficulties met with in studying the behavior of substances at very high temperatures, and of the elaborate experimental devices that are necessary to insure the reliability of the results. Every detail,

no matter how insignificant it may appear, must be carefully studied beforehand in order to avoid all possible sources of error.

The frequent neglect of this last consideration, by the earlier investigators, explains why so many published results need to be thoroughly revised by using the standard methods that have now been developed. The study of the vapor densities of gases that are dissociated at high temperatures, of the specific heats of gases, liquids, and solids under identical circumstances and employing the refined, improved methods of high-temperature measurement, including the exact nitrogen gas thermometer scale, will undoubtedly give us better insight into the true relations existing under these conditions. If my exposition of the chief features of this kind of work shall have contributed somewhat to the completion of that future task, I am glad to have had this opportunity to address you.

PART III

THE CONSTITUTION AND STRUCTURE OF ULTRAMARINE

CHAPTER XX

The Constitution and Structure of Ultramarine

In the course of the work on silicates, being carried on at the laboratory of the University of Groningen, we came across the problem presented by the constitution of the ultramarines. I propose to devote these closing lectures at Cornell University to this subject.

Lazurite, or lapis lazuli, has been one of the most highly prized stones among the semi-precious gems since the earliest times. The ancient Babylonians and the Assyrians valued the stone very highly and compared it, because of its often admixed gold-like pyrite crystals, to the deep blue sky of the oriental night sprinkled with sparkling stars. In the old literature the stone seems to have been confused frequently with the sapphire.

In later years lapis lazuli was imported into Europe from the Orient, more particularly from Afghanistan and from Tibet. It was then highly esteemed for the pigment azure that it furnished. Since the 15th century Europeans have called this pigment "ultramarine", that is, "the substance from beyond the seas". The curious process employed for extracting, from the lapis lazuli, this dark blue pigment with its characteristically warm hue, was described as early as 1271 by Marco Polo. The paint was the most valuable of the blues, was very precious, and its cost rose at times to more than $30 (£6) per pound.[1]

A method for producing ultramarine synthetically was discovered in 1826 by Guimet.[2] Since that time it has been prepared at low cost and in enormous quantities, and—as is

[1] The word "lazurium" is found to occur as far back as the 6th century. It is derived from a Persian word that the Arabian made over into *lazur* or *lazul*. Leonardus wrote in 1502 of *azurum ultramarinum*. The Oriental significance of lapis lazuli is discussed in E. Darmstädter, *Studien zur Geschichte der Chemie* (Lippmann-Festband), p. 1 (Berlin, 1927).

[2] J. B. Guimet, *Bull. Soc. encour. nat.*, 1828; *see also* C. G. Gmelin, *Schweiz. polytechn. J.*, **54**, 360 (1828).

often the case—the chemical synthetic product has far surpassed the natural one, so that today one may obtain blue, red, and violet ultramarines in numberless degrees of tints and hues. Great as has been the progress in their synthesis, however, the problem as to the true constitution of these remarkable substances has not been solved. Ever since the first complete analysis of the substances by Clément and Desormes in 1806,[1] this problem has puzzled chemists and an enormous amount of work on their constitution has been done during the 19th century. But, as we shall soon see, no final success has been attained as yet.

In the following I propose to review the results of a series of investigations during the past two years,[2] made in my laboratory by myself and my two former assistants Dr. H. G. K. Westenbrink and Dr. F. A. van Melle. Their object was to explain the constitution and the structure of the ultramarines. First, however, it will be useful to recall some of the general properties of these substances and the ways in which they are made.

The ultramarines are sodium aluminum silicates that also contain a certain amount of sulphur. They are the products of pyrogenetic processes acting on kaolin mixed with soda, sulphur or sodium sulphate, to which are often added colophonium, coal, or some other reducing agent, the whole being heated to a bright red heat in closed crucibles. After maintaining a constant temperature for 12 to 18 hours, there results a yellowish or greenish mass; this is again glowed in open vessels until it assumes the desired dark blue color. After this the mass is treated with water, which extracts much soluble material, and the remaining ultramarine is washed, decanted, and finally ground.

The principal methods for making the material are three: (1) the sulphate process, in which only sodium sulphate and wood charcoal are mixed with the silicate mass; (2) the mixed soda-sodium-sulphate process, in which the silicate is glowed with a mixture of sodium sulphate, sodium carbonate, sulphur, and tar; (3) the soda process, in which the silicate is mixed with soda, sulphur,

[1] Clément and Desormes, *Ann. chim. phys.*, **57**, 317 (1806).

[2] F. M. Jaeger, *Trans. Faraday Soc.*, **25**, 320ff (1929).

and colophonium and tar. This last method is used, for instance, in the preparation of ultramarines of high silica content. These three processes produce each a material having a different degree of sulphurization. Hoffmann finds that the resulting ultramarines will have, "theoretically", the following compositions:[1]

Sulphate Process	*Sulphate-Soda Process*	*Soda Process*
$Na_{10}Al_6Si_6O_{24}S_2$ *white*	$Na_{12}Al_6Si_6O_{24}S_3$ *white*	$Na_{14}Al_6Si_6O_{24}S_4$ *white*
$Na_8Al_6Si_6O_{24}S_2$ *green*	$Na_9Al_6Si_6O_{24}S_3$ *green*	$Na_{10}Al_6Si_6O_{24}S_4$ *green*
$Na_7Al_6Si_6O_{24}S_2$ *blue*	$Na_7Al_6Si_6O_{24}S_3$ *blue*	$Na_8Al_6Si_6O_{24}S_4$ *blue* (would be the true blue pigment of lapis lazuli; also = $Na_{10}Al_6Si_6O_{24}S_6$)

These different products are seen to be ultramarines of low silica content and having low, medium, and high degrees of sulphurization, respectively. The transformation of the original colorless products into the green and the blue phases corresponds, empirically, to a withdrawal of sodium atoms. Undoubtedly the real mechanism of this transformation involves deeper changes within the mass. In contrast with these ultramarines of low silica content, stand those rich in silica, which have the ratio Al : Si not 1 : 1 but about 1 : 1.5. These silica-rich forms are generally more resistant to alum solutions, contain more than two atoms of sulphur, and as pigments have a deeper, warmer color and greater covering power.

Neither the low-silica nor the high-silica ultramarines have a constant composition corresponding exactly to a stoichiometric formula. In fact it is impossible to obtain products of the same composition even when the experimental conditions are exactly duplicated and the relative amounts of raw materials used are kept the same. In our experiments we got the impression, further, that the composition of the various kinds of ultramarines never can be exactly expressed by a single formula. The reason for this

[1] R. Hoffmann, *Das Ultramarin*, p. 88f, (Braunschweig, 1902).

is, as we shall see, that they are always mixtures of isomorphous and closely related individuals. The ratio of the various components of the mixture depends on the particular circumstances that prevailed during the production of the mixture. The significance of this will become clear later on.

The ultramarines possess a series of remarkable and very characteristic properties.

Toward alkalies they are rather stable, but they are easily decomposed by even very dilute acids. In the latter case a part of the sulphur is set free as such, and another portion is converted into hydrogen sulphide. Blue ultramarine may be heated up to several hundred degrees without being decomposed, only its color is changed to a more greenish hue. When heated with water in sealed tubes up to 300°, sodium sulphide is formed; and according to some observers, a colorless, sulphur-free material is left as residue. So far, we have not been able to confirm this statement.

The ultramarines have the typical character of the so-called permutites. As is the case with those remarkable alumino-silicates,[1] the alkali atoms of the ultramarines may be replaced by other metallic atoms. For instance, silver will almost completely replace them,[2] and the resulting silver ultramarines are yellow. In their turn these silver atoms may be replaced by Na, K, Rb, Cs, Li, Mg, Ca, Sr, Ba, Pb, and so on, by heating with solutions of salts of these metals. In the ordinary ultramarines, also, the Na atoms can be replaced by other metals simply by heating in sealed tubes with solutions of salts of the metals. Towards water all ultramarines behave like potter's clay, thus showing the properties of colloidal pastes; also they have typical hydraulic properties and, as Rohland first demonstrated, they hasten the setting of Portland cement.[3] The sulphur atoms, also, can be replaced by such other elements as Se or Te; the selenium ultra-

[1] F. Singer, *Ueber künstliche Zeolithe.* (Dissertation. Berlin, 1911).

[2] K. Heumann, *Ann.*, 201, 262 (1880); *Ber.*, 10, 991 (1877); J. Szilasi, *Ann.*, 251, 97 (1889); P. G. Silber, *Ber.*, 14, 941 (1881); De Forcrand and Ballin, *Bull. soc. chim.*, 30, 112 (1878); *Compt. rend.*, 88, 30 (1879).

[3] P. Rohland, *Z. angew. Chemie*, 17, 609 (1904).

marines are blood red and the tellurium ultramarines are yellow. These and many other facts indicate clearly, that a considerable number of the constituents of ultramarine are very mobile, just as in the case of the permutites. Moreover, as has been shown by Singer, the latter compounds, when heated with Na_2S or S under special conditions, can be transformed into colored products that partake of the nature of the ultramarines.

The previously known close relationship between the ultramarines and some naturally occurring minerals analogous to the permutites, suggested to us one of our points of attack on the general problem. I refer here to the minerals of the sodalite-hauyne-nosean group. In these minerals, also, a certain portion of their constituents have a high mobility and are easily replaced by other substances, particularly by salts, if heated with their solutions.[1] For this reason these minerals have been often regarded as addition compounds of a sodium-alumino-silicate, having the formula $NaAlSiO_4$, with NaCl in sodalite: $Na_8Al_6Si_6O_{24}Cl_2$; and with Na_2SO_4 or $CaSO_4$ in nosean: $Na_{10}Al_6Si_6O_{32}S_2$; or in hauyne $(Na,Ca)_{10}Al_6Si_6O_{32}S_2$; and finally, with Na_2CO_3 or $CaCO_3$ in cancrinite: $(Ca,Na)_{10}Al_8Si_8O_{32}(CO_3)_2 + 3H_2O$.[2] It must be remarked that in nature, also, the composition of these minerals is never constant. Nosean and hauyne, for example, contain variable amounts of $CaSO_4$ and Na_2SO_4, the Ca evidently replacing two Na atoms isomorphously, while between the two minerals there are all possible transitional members, so that their differences are more quantitative than qualitative in nature. Lemberg's syntheses indicate that the fundamental silicate of all these minerals is closely related to nepheline or one of its hydrates. All these minerals may be transformed into one another by heating them with solutions of Na_2SO_4, NaCl, Na_2CO_3, and the like.[3] The analogy

[1] J. Lemberg, *Z. geol. Ges.*, **28**, 603 (1876); **35**, 583, 590 (1883); J. Morozewicz, *Tschermak min. Mitth.*, **18**, 131, 143 (1899); S. J. Thugutt, *Neues Jahrb. Mineral. Geol.*, Beil. Bd. **9**, 568 (1894); S. Weyberg, *Z. Kryst.*, **53**, 612 (1914); W. C. Brögger and H. Bäckström, *Z. Kryst.*, **18**, 209 (1890); and others.

[2] The exact formula of cancrinite is doubtful; its symmetry also is different from that of the other minerals.

[3] Lemberg, *Z. deut. geol. Ges.*, **35**, 590 (1883); **40**, 625 (1888); etc.

between lazurite, sodalite, nosean, hauyne, ultramarine, and the alkali-lime garnets was specially pointed out by Brögger and Bäckström in 1890,[1] and they also tried to isolate the blue pigment in a pure state from lazurite. Using the formulas with 3Al and 3Si, for the sake of simplicity, in place of Al_6Si_6, the following formulas represent the way in which they expressed the supposed connection:

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_4\\Al\\Al-Cl\end{matrix}$$

sodalite.

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_2\\Ca\\Al\\Al(SO_4Na)\end{matrix}$$

nosean, hauyne.

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_4\\Al\\Al-S_3Na\end{matrix}$$

ultramarine.

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_4\\Ca\\Al\end{matrix}$$

alkali-lime garnet.

We shall see, however, that neither sodalite nor garnet belong to the same structural group as nosean (hauyne) and the ultramarines.

Other investigators[2] have supposed that nephelite is the mother-silicate of this whole class of compounds, and have tried to use Werner's co-ordination theory to express the relationships, as follows:

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_2\\Al_2\end{matrix}$$

nephelite.

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_3\\Al_2\ldots CaSO_4\end{matrix}$$

hauyne, nosean.

$$\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_3\\Al_2\ldots NaCl\end{matrix}$$

sodalite.

$$\left[\left\{Al(SiO_4)_3\right\}\begin{matrix}Na_3\\Al_2\end{matrix}\right]_2\ldots 2NaS_2.$$

natural ultramarine.

Here again the same arguments may be adduced against placing all these compounds in the same group;[3] moreover, it will be shown in the following that nephelite cannot be considered the underlying mother-silicate.[4] In general W. L. Bragg's recent determinations of the structures of

[1] *Op. cit.*

[2] J. Jacobs, *Z. anorg. Chem.*, 106, 229 (1919); *Helv. Chim. Acta*, 3 ,669 (1920); E. Gruner, *Z. angew. Chem.*, 41, 447 f. (1928).

[3] G. Menzer, *Centr. Mineral. Geol.*, **A**, 344 (1925); **A**, 343 (1926); *Ztschr. Kryst.*, 63, 157 (1926).

[4] N. L. Bowen, *Am. J. Sci.*, (4) 33, 49, 551 (1912); (4) 43, 115 (1917).

the silicates seem to indicate that it is vain to write such formulas for crystallized silicates, since they are rather to be regarded as orderly aggregations of atoms or electrically charged ions.

The true symmetry of the ultramarines is not yet known with certainty. Undoubtedly they are, in common with sodalite, hauyne, and nosean, all cubic and probably ultramarines of different compositions may slightly differ in symmetry within the cubic system. Sodalite shows a cleavage parallel with (110); nosean may have an imperfect one parallel with (111). The predominant crystal habit both of ultramarine[1] and of the above is the rhombic dodecahedron (110), with frequent twinning on (100) in all cases.[2] Some observations by Brögger and Bäckström seem to prove that the symmetry of sodalite is hexakistetrahedral rather than holohedral, the apparently simple rhombic dodecahedra being actually twins on (100). We shall see that the structure of sodalite is certainly different from that of nosean, hauyne and the ultramarines.

Heumann studied the substitution of silver by the alkali metals in the silver ultramarines, and also that of sodium by silver in the ordinary ultramarines.[3]

When the ultramarine is digested with an ammoniacal solution of AgCl for several days, on the water bath, the sodium of the original compound is replaced in part by silver. Heumann thought that two-thirds of the original sodium atoms were finally thus replaced by silver. It is demonstrable, however, that this is not the case; that the degree of replacement is variable and is not to be represented by a simple chemical formula, because it varies with the concentration of the solutions, the duration of the heating, and with absorption phenomena dependent upon the degree of subdivision of the ultramarine used. The same is true for silver ultramarine heated with solutions of the alkali-halogenides in a flask with reflux-cooler. According

[1] F. Fischer, *Dinglers polytech. J.*, **221**, 562 (1876); T. Morel, *Mon. sci.*, 785 (1879); C. Grünzweig and R. Hoffmann, *Ber.*, **9**, 864 (1876); W. C. Brögger and H. Bäckström, *op. cit.*, 242.

[2] F. M. Jaeger, H. G. K. Westenbrink, and F. A. van Melle, *Proc. Acad. Sci. Amsterdam*, **30**, 250 (1927).

[3] K. Heumann, *Ann.*, **199**, 253 (1879); **201**, 262 (1880); **203**, 174 (1881).

to Heumann this reaction would continue only until two-thirds of the silver atoms were replaced by alkali; but we found this not to be the case, even though the silver compound be heated at 120°–160° for a long time with a great excess of the alkali-halogenides in sealed tubes. In illustration we may here briefly consider the results of four series of experiments instituted to check this conclusion. In the first series (A) 7 gm. ultramarine (Guimet-7553, silica-rich), 24 gm. sodium iodide, and 10 gm. water, were placed in sealed tubes and heated at 100° in a thermostat for various lengths of time. On opening the tubes after, 1, 2, 3, up to 50 hours of heating, the contents were thoroughly washed and the silver content of the product was determined. A second series of experiments (B) was started using a concentration just half of that for series A; in the third series (C) the concentration of the solution was but one-third that used in series A; and in a fourth series (D) the same concentration as that used in series A, was kept at the higher constant temperature of 160°. The results of the four series are shown in Table XXXVII, and presented graphically in Figure 134.

TABLE XXXVII

Results of four Substitution Experiments with Silver Ultramarines

Time of Heating in Hours:	Percentage of original Silver substituted:			
	Series A	Series B	Series C	Series D
1	32	30	——	——
2	48	46	——	——
3	52.5	50.6	——	——
4	58	55.7	——	——
5	60.7	58.2	46	94.9
6	63	60	——	——
7	64.5	62	——	——
8	65.7	63.3	——	——
9	67	64.5	——	——
10	68	65.7	52.5	——
15	72.7	70.3	——	——
23	76.6	74.5	——	——
36	81	79	——	——
50	84.5	81.6	——	97.7

Figure 134 makes it evident at once that:

(a) Substitution goes on more rapidly during the first part of the process, being more rapid for the higher concentrations (Series C, B, A) and temperatures (Series A, D).

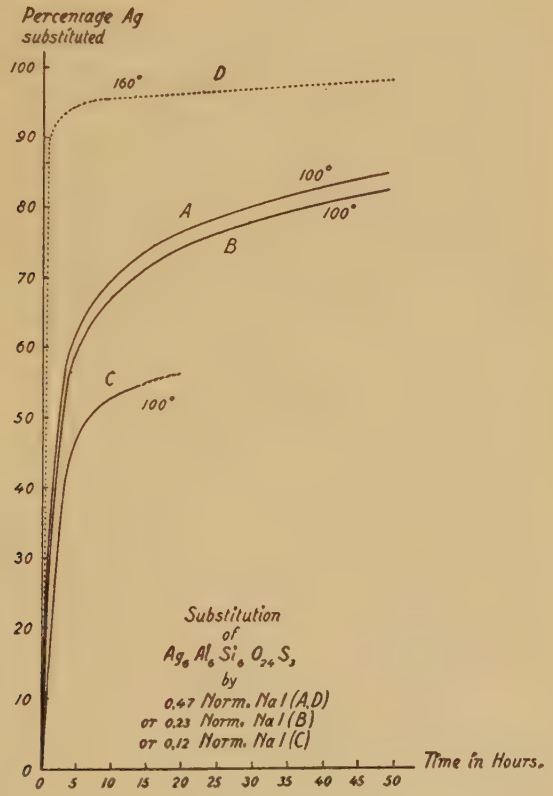


FIG. 134

(b) All the curves are analogous in shape and typical of surface reactions, where the surface gradually comes to saturation. Saturation is attained more rapidly when the temperature is higher (Curves *D* and *A*).

We repeated the experiments in sealed tubes at a temperature of 130°, using five-fold quantities of LiCl, NaCl, KCl, RbCl, CsCl, $(NH_4)Cl$; and at 160° using the same

excess of LiI, NaI, KI, RbI, CsI, and $(NH_4)I$, all in the same concentrations.[1] It was found that:

(1) With equal molar concentrations of the salt solutions, silver is replaced by the alkali metals to an appreciably greater extent—other things being equal—when the iodides are used, than with the chlorides. This is certainly due to the relatively lower solubility of AgI compared with AgCl.

(2) The alkali metals replace the silver more completely as the concentrations increase.

(3) Under equal conditions of temperature, concentration and duration of heating, the silver is replaced more rapidly and completely as the atomic weight of the alkali metal decreases. Replacement is most rapid and complete with lithium, followed in decreasing order by Na, K, Rb, and Cs. Ammonium (NH_4) is about equivalent to K in its action.

The above results demonstrate completely that there is no upper limit of substitution for alkali atoms replacing silver atoms. The only question here is that of equilibria, of conditions that are gradually attained, depending on the concentration of the salt solutions and the special nature of the ions to be introduced into the ultramarines. This behavior is quite analogous with that of the permutites when brought into contact with solutions of salts.

Analogous phenomena are observed when silver ultramarine is melted up in a crucible with an excess of the halogenides of other metals. Heumann thought that under such conditions all the silver was replaced by the alkali atoms present, the product being beautifully colored ultramarines. We found this conclusion to be erroneous. The products thus obtained always contained some silver, the amount depending on the particular halogenide that was used, the degree of its excess, and the melting temperature. Even when 30 or 40 times the theoretical amounts of the salts were used, we found the reactions never complete. It is a remarkable fact that, on using the silver

[1] The resulting products must be freed from AgCl, or AgI, by treating with a 10-percent solution of KCN; and from traces of sulphur by extracting with CS_2. No appreciable amounts of SiO_2 or of Al_2O_3 were found in the filtrates in this case.

compounds of green, red, and violet ultramarines, the regenerated ultramarines were always blue.

Concerning the preparation of the silver ultramarines, it may be recalled that Heumann started with an ultramarine poor in silica, and obtained a yellow silver ultramarine to which he ascribed the formula: $Ag_6Al_6Si_6O_{24}S_2$. We started with Guimet-blue No. 7553, whose composition is very nearly $Na_6Al_4Si_6O_{24}S_3$, it being an ultramarine rich in silica. This ultramarine was heated with a large excess of $AgNO_3$ at 120°, in a sealed tube, for 50 hours. After purifying with KCN and removing the remaining Ag_2S by repeated decantation, it was found that the yellow silver ultramarine obtained always contained some sodium, and that it was also a derivative of the low-silica series. In the filtrate we found considerable quantities of SiO_2 and Al_2O_3 in addition to Ag_2SO_4, Ag_2S (in the KCN extract), and $NaNO_3$. Evidently there had been a partial decomposition of the silica-rich ultramarine under the influence of the hydrolyzation products of the silver nitrate, and the more stable silver salt of an ultramarine where Al : Si = 1 : 1 had been generated. These reactions require more detailed study.

Our experiments for studying the structure proper of these remarkable substances may now be discussed. The problem was attacked by means of X-rays. As ultramarines cannot be obtained in well-developed crystals, we have had to rely on powder-spectrograms made by means of copper α-radiation. As the ultramarines are closely related to sodalite, nosean, and hauyne, of which excellent crystals were available from Monte Somma, Niedermendig, Laacher See, and elsewhere, we made X-ray studies of these minerals also, at the same time. For the ultramarines we used the ultramarine blue prepared by the Usines d'Outremer-Guimet (Fleurieu), and a number of pink, red, green, blue and violet preparations from the Vereinigte Ultramarin-Fabriken (Köln). Among these different products some had a low and some a high silica content; some showed relatively high sulphurization (S_3), some lower (S_2), and the like.

The first really striking fact that we discovered was that all ultramarines—as well as nosean and hauyne—gave identical powder-spectrograms, quite independently of their color and chemical composition. Sodalite, on the other hand, showed a quite different spectrogram. These important facts are supported by the observational results set forth in Tables XXXVIII, XXXIX, and XL.

In the case of those ultramarines, nosean, and hauyne, that we studied (h+k+l) appears never to have been an odd number for any of the observed diffraction lines; this makes the impression, at first, that the fundamental lattice is here the body-centered cubic one with an edge of the cube-cell equal to 9.13Å. The elementary cell of nosean contains $Na_{10}Al_6Si_6O_{32}S_2$ in the simplest case, while in the ultramarine but one molecule that has 6 Si atoms is present within the cell of their structures. In the case of sodalite the structure apparently is different, the lattice being the simple cubic one with an edge a_0 of 8.81Å. Its elementary cell contains the mass: $Na_8Al_6Si_6O_{24}Cl_2$.

TABLE XXXVIII

Powder-Spectrograms of Nosean, Hauyne and Eight Different Ultramarines.

Number of Image	Estimated Intensity	2l in mm.	λ	½θ	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {hkl}
1	1	16.8	α	9°37′	0.0279	0.0284	(200)
2	1	19.0	β	10°53′	0.0356	0.0352	(211)
3	8	21.0	α	12° 2′	0.0433	0.0426	(211)
4	5	27.0	α	15°28′	0.0711	0.0710	(310)
5	5	29.7	α	17° 4′	0.0861	0.0852	(222)
6	1	34.5	α	19°49′	0.1149	0.1136	(400)
7	3	36.5	α	20°58′	0.1280	0.1278	(330)
8	3	44.5	α	25°33′	0.1860	0.1846	(431)
9	2	49.5	α	28°25′	0.2265	0.2272	(440)
10	1	51.3	α	29°27′	0.2417	0.2414	(530)
11	1	53.0	α	30°22′	0.2556	0.2556	(600)
12	1	54.8	α	31°24′	0.2715	0.2698	(532)
13	1	59.5	α	34° 9′	0.3151	0.3124	(622)

Radius of Camera: 25 mm. V = ca. 55000 volts. Time of Exposure: 3 hours.

Wave-length: $\lambda_{Cu} = 1.540$ Å $\lambda\beta = 1.388$ Å.

Quadratic Equation: $\sin^2\frac{1}{2}\theta = 0.0071(h^2+k^2+l^2)$; $a_0 = 9.13$ Å.

TABLE XXXIX

Powder-Spectrogram of Ultramarine rich in Silica.

(GUIMET III, No. 7553)

Number of Image	2l in mm.	Estimated Intensities	λ	$\Sigma(\overline{h^2})$	$\frac{1}{2}\theta$	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {hkl}
1	21.4	4?	α	2	6°54′	0.0144	0.0144	(110)*
2	37.1	10	α	6	11°58′	0.0430	0.0432	(211)
3	43.6	1	β	10	14° 4′	0.0591	0.0590	(310)
4	48.2	7	α	10	15°33′	0.0719	0.0720	(310)
5	53.0	8	α	12	17° 6′	0.0865	0.0864	(222)
6	55.4	1⁻	β	16	17°52′	0.0941	0.0944	(400)
7	57.1	2	α	14	18°25′	0.0999	0.1008	(321)
8	59.0	1⁻	β	18	19° 2′	0.1063	0.1062	(330); (411)
9	61.5	4	α	16	19°50′	0.1151	0.1152	(400)
10	65.4	5	α	18	21° 6′	0.1296	0.1296	(330); (411)
11	71.3	1⁻	β	26	23° 0′	0.1528	0.1534	(431); (510)
12	72.9	1	α	22	23°31′	0.1590	0.1584	(332)
13	79.6	5	α	26	25°41′	0.1877	0.1872	(431); (510)
14	82.4	1⁻	β	34	26°35′	0.2004	0.2006	(433); (530)
15	86.0	1	α	30	27°44′	0.2165	0.2160	(521) as β-line (600)
16	89.2	3	α	32	28°47′	0.2317	0.2304	(440)
17	92.0	2	α	34	29°41′	0.2451	0.2448	(433); (530)
18	95.0	2	α	36	30°39′	0.2599	0.2592	(600)
19	97.9	2	α	38	31°35′	0.2742	0.2736	(532); (611)
20	106.4	3	α	44	34°20′	0.3180	0.3168	(622)
21	109.1	1⁻	β	56	35°12′	0.3322	0.3304	(642) as α-line (631)
22	111.9	2	α	48	36° 6′	0.3471	0.3459	(444)
23	114.7	1	α	50	37° 0′	0.3621	0.3600	(543); (505); (710)
24	120.0	2	α	54	38°43′	0.3910	0.3888	(633); (721)
25	122.1	1	α	56	39°23′	0.4026	0.4032	(642)
26	124.8	1	α	58	40°16′	0.4178	0.4176	(730)
27	130.2	1	α	62	42° 0′	0.4476	0.4464	(732)
28	132.8	1	α	64	42°50′	0.4620	0.4608	(800)
29	135.0	1	α	66	43°33′	0.4747	0.4752	(554); (741); (811)
30	145.5	1	α	74	46°56′	0.5337	0.5328	(750); (743); (831)
31	148.4	1	α	76	47°51′	0.5498	0.5472	(662)
32	150.9	1	α	78	48°41′	0.5640	0.5616	(752)
33	153.5	1	α	80	49°31′	0.5785	0.5760	(840)

Radius of Camera: 44.4 mm. V = 55000 volts.
Time of Exposure: 2 hours.

Wave-length: $\lambda_\alpha = 1.540$ Å. $\lambda_\beta = 1.388$ Å.

Quadratic Equation: $\sin^2\frac{1}{2}\theta = 0.007\frac{1}{2}(h^2+k^2+l^2)$ (α-radiation);

$a_0 = 9.12$ Å.

$\sin^2\frac{1}{2}\theta = 0.0059(h^2+k^2+l^2)$ (β-radiation).

* This intensity is certainly higher, but the line falls within the central halo and its intensity cannot be estimated accurately.

TABLE XL

Powder-Spectrogram of Sodalite (Monte Somma).

Number of Image:	Estimated Intensities	2l in mm.	λ	$\frac{1}{2}\theta$	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {hkl}
1	1	23.1	β	13°14′	0.0524	0.0503	(220)
2	8	25.5	α	14°37′	0.0637	0.0608	(220)
3	2	31.2	α	17°53′	0.0943	0.0912	(222)
4	3	34.3	α	19°39′	0.1131	0.1064 or 0.1216	(321); (400)
5	3	37.5	α	21°29′	0.1341	0.1368	(330)
6	3	41.3	α	23°40′	0.1611	0.1596	(421)
7	3	42.3	α	24°14′	0.1685	0.1672	(332)
8	1	50.1	α	28°43′	0.2309	0.2280	(521)
9	1	53.0	α	30°25′	0.2563	0.2584	(530)
10	1	56.3	α	32°16′	0.2850	0.2812 or 0.2888	(601); (611)

Radius of Camera: 25 mm. V = 55000 volts.
Time of Exposure: 3 hours.
Quadratic Equation: $\sin^2\frac{1}{2}\theta = 0.0076\,(h^2+k^2+l^2)$, for α-radiation.
$a_0 = 8.81$ Å.

TABLE XLI.

Rotation-spectrogram of Nosean when turned about [111].

(Distance of Plate to Crystal: 40 mm.)

Distance of Center to Image	$\frac{1}{2}\theta$	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {hkl}	Hyperbola
18.0	12° 7′	0.0441	0.0426	$(2\bar{1}1)$	Principal spectrum
30.0	18°26′	0.1000	0.0994	$(3\bar{2}1)$	
36.0	21° 0′	0.1284	0.1278	$(3\bar{3}0)$	
49.5	25°32′	0.1860	0.1846	$(4\bar{2}2)$	
62.5	28° 0′	0.2304	0.2272	$(4\bar{4}0)$	
18.0	12° 7′	0.0441	0.0426	$(2\bar{1}\bar{1})$	Ist
24.0	15°29′	0.0731	0.0710	$(3\bar{0}\bar{1})$	
41.5	23° 2′	0.1531	0.1562	$(3\bar{2}\bar{3})$	
49.5	25°32′	0.1860	0.1846	$(4\bar{1}\bar{3})$	
66.0	29°23′	0.2407	0.2414	$(3\bar{3}\bar{4})$; $(5\bar{0}\bar{3})$	
17.5	11°49′	0.0419	0.0426	(211)	IInd
24.0	15°29′	0.0713	0.0710	(310)	
33.0	19°46′	0.1144	0.1136	(400)	
30.0	18°26′	0.1000	0.0994	(321)	IIIrd
36.0	21° 0′	0.1284	0.1278	(330)	
49.5	25°32′	0.1860	0.1846	$(43\bar{1})$	
41.5	23° 2′	0.1531	0.1562	(332)	IVth
49.5	25°32′	0.1860	0.1846	(431)	

Wave-length: $\lambda_{Cu} = 1.540$ Å; V = 55000 volts; Exposure: 5 hours.

The above measurements show that hauyne, nosean, and all the ultramarines, if not identical in structure, at any rate have a certain predominant spectrographic characteristic in common. We then utilized the macroscopic crystals of nosean and hauyne for the more detailed studies of the structure by means of rotation-spectrograms and simple spectrograms on different planes. Most of the crystals at our disposal were twinned, and all were too small for Laue-spectrograms to be prepared.

In the case of hauyne we found that we could obtain an image of the first order on (110). Using rock salt as a standard, $d_{(100)}$ appeared to be 9.11Å.

In the case of nosean, $d_{(100)}$ was determined as 9.13Å; and furthermore the spacing parallel to (111) was halved. This latter fact is in agreement with the presence of a body-centered cubic cell.

A simple, untwinned crystal of nosean permitted the preparation of a rotation-spectrogram with [111] as the axis of rotation, this is analyzed in Table XLI. It will be noted that the sum of the indices of the principal spectrum is zero, that the corresponding figure for the first hyperbola is 2, for the second hyperbola is 4, for the third hyperbola is 6, and so on. All images {h k l} in odd orders have the intensity zero when (h+k+l) is odd. This observation was confirmed by a spectrogram on (111), for which the plate was exposed a full hour; this gave the second-order image in considerable intensity, but not the faintest trace of the first-order image was to be detected.

The convincing data of Table XLII corroborate our views. The data were obtained from small, untwinned crystals of hauyne and nosean, rotating them about a principal axis [100].

These spectrograms were analyzed by Bernal's graphic method.[1] The corresponding data for sodalite, when rotated about [001], are given in Table XLIII.

These data give the spacing $d_{(100)}$ for sodalite as 8.72Å, a value in good agreement with the exact value, 8.81, previously deduced for sodalite.

[1] J. D. Bernal, *Proc. Roy. Soc. London*, **A113**, 117 (1927).

TABLE XLII

Rotation-Spectrograms of Nosean and Hauyne, if turned about a principal axis [100].

Nosean Images	Hauyne Images
Principal Spectrum:	Principal Spectrum:
$\lambda\alpha$: $(0\bar{3}1)$; $(0\bar{5}1)$; $(0\bar{4}0)$; (031); (033); (051).	$\lambda\alpha$: $(0\bar{1}3)$; (004); (015); $(03\bar{3})$; (053).
$\lambda\beta$: $(0\bar{5}3)$; (053); (033).	$\lambda\beta$: (004); (035); $(03\bar{3})$.
1st Access. spectrum:	1st Access. spectrum:
$\lambda\alpha$: $(1\bar{3}2)$; $(1\bar{5}0)$; (121); (132); (150); (152).	$\lambda\alpha$: $(1\bar{1}3)$; (105); $(15\bar{2})$; (121); $(13\bar{2})$; $(14\bar{3})$.
$\lambda\beta$: (150).	$\lambda\beta$: (121); $(14\bar{3})$.
−1st Access. spectrum:	−1st Access. spectrum.
$\lambda\alpha$: $(\bar{1}50)$; $(\bar{1}32)$; $(\bar{1}50)$; $(\bar{1}52)$.	$\lambda\alpha$: $(\bar{1}\bar{1}3)$; $(\bar{1}05)$; $(\bar{1}52)$; $(\bar{1}2\bar{1})$; $(\bar{1}3\bar{2})$; $(\bar{1}4\bar{3})$.
$\lambda\beta$: $(\bar{1}21)$; $(\bar{1}50)$.	$\lambda\beta$: $(\bar{1}4\bar{3})$.
2d Access. spectrum:	2d Access. spectrum:
$\lambda\alpha$: $(23\bar{1})$; (233); (242).	$\lambda\alpha$: (213); (215); $(21\bar{1})$; $(22\bar{2})$; $(23\bar{3})$; $(24\bar{2})$.
$\lambda\beta$: (222).	$\lambda\beta$: (253); (235).
−2d Access. spectrum:	−2d Access. spectrum:
$\lambda\alpha$: $(\bar{2}3\bar{1})$; $(\bar{2}20)$; $(\bar{2}33)$; $(\bar{2}42)$.	$\lambda\alpha$: $(\bar{2}13)$; $(\bar{2}15)$; $(\bar{2}2\bar{2})$; $(\bar{2}3\bar{3})$; $(\bar{2}4\bar{2})$.
$\lambda\beta$: $(\bar{2}22)$.	$\lambda\beta$: $(\bar{2}2\bar{2})$; $(\bar{2}5\bar{3})$.
3d Access. spectrum:	3d Access. spectrum:
$\lambda\alpha$: $(33\bar{2})$; (310); (321); (332).	$\lambda\alpha$: (312); (303); (314); (310); $(32\bar{1})$; $(33\bar{2})$; (350).
$\lambda\beta$: (350); (352).	$\lambda\beta$: $(35\bar{2})$; (350).
−3d Access. spectrum:	−3d Access. spectrum:
$\lambda\alpha$: $(\bar{3}4\bar{1})$; $(\bar{3}10)$; $(\bar{3}50)$; $(\bar{3}52)$.	$\lambda\alpha$: $(\bar{3}12)$; $(\bar{3}03)$; $(\bar{3}14)$; $(\bar{3}05)$; $(\bar{3}10)$; $(\bar{3}2\bar{1})$; $(\bar{3}3\bar{2})$; $(\bar{3}50)$.
$\lambda\beta$: $(\bar{3}3\bar{1})$.	$\lambda\beta$: $(\bar{3}03)$; $(\bar{3}50)$; $(\bar{3}5\bar{2})$.
4th Access. spectrum:	4th Access. spectrum:
$\lambda\alpha$: $(43\bar{1})$; (431).	$\lambda\alpha$: (422); (413); $(43\bar{1})$; (420).
$\lambda\beta$: $(44\bar{0})$.	$\lambda\beta$: (404); $(43\bar{1})$.
−4th Access. spectrum:	−4th Access. spectrum:
$\lambda\alpha$: $(\bar{4}3\bar{1})$; (431); $(\bar{4}20)$; (422).	$\lambda\alpha$: $(\bar{4}22)$; $(\bar{4}13)$; $(\bar{4}20)$; $(\bar{4}2\bar{2})$; $(\bar{4}31)$.
$\lambda\beta$: $(\bar{4}40)$.	$\lambda\beta$: $(\bar{4}3\bar{1})$; $(\bar{4}13)$; $(\bar{4}04)$.

TABLE XLIII

Rotation-Spectrogram of Sodalite, if turned about [001]

(Distance of plate to crystal: 40.5 mm.)

Distance of Image to Center of Film	$\frac{1}{2}\theta$	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {hkl}	Hyperbola:
25.3	16° 0′	0.0760	0.0760	(310)	
32.0	19° 9′	0.1076	0.1131	(330) $\lambda\beta$	
38.9	21°56′	0.1395	0.1368	(330) $\lambda\alpha$	Principal spectrum.
42.0	23° 1′	0.1529	0.1520	(420)	
52.0	26° 3′	0.1927	0.1900	(500); (430)	
64.1	28°51′	0.2328	0.2204	(520)	
70.0	29°59′	0.2496	0.2432	(440)	
18.7	12°24′	0.0461	0.0456	(211)	
31.5	18°56′	0.1053	0.1064	(321)	Ist
39.1	22° 0′	0.1402	0.1368	(411)	
52.0	26° 3′	0.1928	0.1976	(501); (431)	
18.7	12°24′	0.0461	0.0456	(112)	
24.0	15°9½′	0.0684	0.0699	(212)	
28.0	17°20′	0.0888	0.0912	(222)	
32.1	19°12′	0.1081	0.1064	(312)	
39.0	23°41′	0.1613	0.1596	(412)	IInd
48.0	24°55′	0.1775	0.1824	(422)	
62.5	28°32′	0.2282	0.2204	(432)	
75.0	30°49′	0.2625	0.2508	(522)	
82.0	31°51′	0.2785	0.2736	(442)	
25.8	16°15′	0.0783	0.0760	(103)	
31.8	19°41′	0.1067	0.1064	(123)	
37.9	21°33′	0.1348	0.1368	(303)	IIIrd
45.6	24°12′	0.1682	0.1672	(233)	
72.0	30°20′	0.2553	0.2584	(433); (503)	
48.6	25° 6′	0.1799	0.1824	(224)	
55.8	27° 1′	0.2063	0.2010	(314)	IVth
77.9	31°16′	0.2694	0.2628	(334)	

Wave-length: $\lambda_{Cu} = 1.540$ Å: V = 55000 volts.
Time of exposure: 5 hours.
Quadratic equation: $\sin^2\frac{1}{2}\theta = 0.0076(h^2+k^2+l^2)$.
$a_0 = 8.81$ Å.

Before we employ the above data in discussing the structure, we would mention some results of spectrographic investigations of the corresponding silver ultramarines, mixed ultramarines, and selenium ultramarines.

In preparing the silver ultramarines we started with silica-rich Guimet-7553, whose composition was approximately $Na_6Al_4Si_6O_{24}S_3$, and heated it to 130° for 50 hours in a sealed tube with a great excess of $AgNO_3$ and water. The resulting yellow silver ultramarine was found, upon analysis, to contain Ag = 41.3 per cent, Na = 2.6 per cent, Si = 10.9 per cent, Al = 10.4 per cent, and S = 6.7 per cent, hence O = 28.1 per cent. The analysis of these substances is very tedious, and the amount of oxygen is always uncertain because it contains all the accumulated errors. It is only in recent times that sodium has been found to occur in them and that it is present not as an impurity, but as an essential constituent. The composition agrees very closely with the formula: $Ag_6Na_2Al_6Si_6O_{28}S_3$ whence it is clear that, as has been pointed out, there must have been a profound decomposition of the original ultramarine in this reaction; indeed we could prove that the filtrate contained Ag_2SO_4, $NaNO_3$, SiO_2, while NO_2 and Ag_2S were also formed. Perhaps we might write the reaction as follows:

$$3Na_6Al_4Si_6O_{24}S_3 + 18AgNO_3 + nH_2O = 2Ag_6Na_2Al_6Si_6O_{28}S_3 + 14NaNO_3 + Ag_2S + 2Ag_2SO_4 + 6SiO_2 + 4NO_2 + nH_2O.$$

It appeared that this silver ultramarine, as well as all other silver ultramarines prepared from otherwise-colored ultramarines—though these certainly had a composition differing from $Ag_6Na_2Al_6Si_6O_{28}S_3$—showed identical powder-spectrograms. Although these differed from those of the sodium ultramarines in the matter of the relative intensities of the diffraction lines, yet they still had the true character of the ultramarine spectra. In Table XLIV are given the results of the analysis of the above silver-compound. The results from a very sharp powder-spectrogram of a silver ultramarine derived from a low-silica green ultramarine (V-U-F, X) are given in Table XLV.

These data show that, in spite of the widely different silver-content (41 and 51 per cents), the spectra are all the

same, and that although the original ultramarine type has been preserved the lattice-constant, a_0, has been diminished to about 8.93Å. The most pronounced differences between the intensities of corresponding diffraction images in sodium and silver ultramarines are that in silver ultramarine the intensity of (310) is always greater than those of (211) and (222), the strongest lines in the spectra of the sodium ultramarines.

Regarding the mixed ultramarines, those containing sodium and silver in varying proportions, it may be stated that the value of a_0 decreases gradually as the percentage of silver increases. This is readily seen in the following:

For 0 per cent silver, a_0 = 9.11 Å
" 7·75 " " , = 9.03
" 31.6 " " , = 9.00
" 39·4 " " , = 9.00
" 46.5 " " , = 8.96 to 8.99
" 51 " " , = 8.93

TABLE XLIV

Silver Ultramarine derived from Guimet-7553.

Image No.	Estimated Intens.	Radiation	2l mm.	$\frac{1}{2}\theta$	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {h k l}
1	5	α	37.2	12° 0′	0.0432	0.0440	(211)
2	5	β	43.6	14° 4′	0.0591	0.0596	(310)
3	9	α	48.6	15°39′	0.0728	0.0733	(310)
4	5	α	53.4	17°14′	0.0878	0.0880	(222)
5	4	α	57.5	18°33′	0.1012	0.1025	(321)
6	2	β	59.2	19° 6′	0.1071	0.1073	(330); (411)
7	9	α	66.1	21°19′	0.1321	0.1319	(330); (411)
8	1	β	81.1	26°16′	0.1958	0.1907	(440)
9	2	β	87.6	28°16′	0.2243	0.2282	(611); (532)
10	3	α	90.0	29° 3′	0.2358	0.2346	(440)
11	5	α	93.0	30° 0′	0.2500	0.2493	(433); (530)
12	3	α	95.7	30°52½′	0.2633	0.2638	(600)
13	4	α	98.6	31°48½′	0.2778	0.2785	(611); (532)
14	2	α	101.6	32°46½′	0.2931	0.2932	(620)
15	1	β	107.4	34°39′	0.3233	0.3218	(633); (721)
16	1	β	112.4	36°16′	0.3499	0.3458	(730)
17	5	α	120.9	39° 0′	0.3960	0.3958	(633); (721)
18	2	α	126.1	40°41′	0.4250	0.4251	(730)

Radius of camera: 44.4 mm. V = 55000 volts. Exposure: 3 hours.
Wave-length: λ_α = 1.540Å; λ_β = 1.388Å;
Quadratic equation: $\sin^2\frac{1}{2}\theta = 0.00733(h^2+k^2+l^2)$ for α-radiation
$\sin^2\frac{1}{2}\theta = 0.00596(h^2+k^2+l^2)$ for β-radiation
a_0 = 8.99Å.

TABLE XLV.

Silver Ultramarine derived from Green Ultramarine, V-U-F,X.

Image No.	2l mm.	Intensities	λ	½θ	$\sin^2\frac{1}{2}\theta$ (observed)	$\sin^2\frac{1}{2}\theta$ (calculated)	Indices {h k l}
1	34.6	2	β	11°10′	0.0374	0.0362	(211)
2	37.5	5	α	12° 6′	0.0439	0.0446	(211)
3	43.7	3	β	14° 6′	0.0593	0.0604	(310)
4	49.7	8	α	16° 2′	0.0763	0.0743	(310)
5	53.1	1	β	17° 8′	0.0868	0.0846	(321)
6	54.5	4	α	17°35′	0.0913	0.0892	(222)
7	58.9	3	α	18°58′	0.1056	0.1040	(321)
8	60.3	2	α	19°27′	0.1108	0.1179	(400)
9	64.3	1	β	20°44′	0.1252	0.1208	(420)
10	67.0	8	α	21°37′	0.1358	0.1337	(330); (411)
11	70.8	3	α	22°50′	0.1505	0.1486	(420)
12	74.4	2	α	24° 0′	0.1655	0.1635	(332)
13	77.9	4	α	25° 8′	0.1804	0.1783	(422)
14	81.2	4	α	26°12′	0.1950	0.1922	(431); (510)
15	84.1	2	β	27° 8′	0.2080	0.2054	(433); (530)
16	86.3	1	β	27°50′	0.2180	0.2174	(600)
17	90.8	3	α	29°17′	0.2391	0.2378	(440)
18	93.8	5	α	30°16′	0.2541	0.2526	(433); (530)
19	97.0	3	α	31°18′	0.2699	0.2675	(600)
20	99.7	4	α	32°10′	0.2835	0.2823	(532); (611)
21	102.6	2	α	33° 6′	0.2983	0.2972	(620)
22	105.6	2	α	34° 4′	0.3138	0.3121	(541)
23	108.4	2	α	34°58′	0.3284	0.3269	(622)
24	110.7	1	α	35°43′	0.3408	0.3418	(631)
25	113.7	1	α	36°41′	0.3569	0.3566	(444)
26	115.6	1	α	37°17′	0.3670	0.3715	(543); (505); (701)
27	121.9	5	α	39°19′	0.4014	0.4012	(633); (721)
28	127.3	2	α	41° 4′	0.4315	0.4309	(730)
29	132.5	1	α	42°44′	0.4605	0.4607	(732)
30	137.8	1	α	44°28′	0.4906	0.4904	(554); (741); (811)
31	140.4	1	α	45°17′	0.5049	0.5052	(644); (820)
32	143.2	1	α	46°12′	0.5210	0.5201	(653)
33	145.5	1	α	46°56′	0.5338	0.5350	(660); (822)
34	148.4	1	α	47°53′	0.5503	0.5499	(750); (743); (831)
35	150.9	1	α	48°41′	0.5641	0.5647	(662)
36	153.7	1	α	49°35′	0.5796	0.5795	(752)
37	155.9	1	α	50°17′	0.5917	0.5944	(840)
38	158.8	1	α	51°14′	0.6080	0.6093	(833)
39	164.4	1	α	53° 2′	0.6383	0.6390	(655)
40	169.7	1	α	54°45′	0.6669	0.6687	(851)

Radius of camera: 44.4 mm. V = 55000 volts. Exposure: 3 hours.
Wave-length: λ_α = 1.540Å; λ_β = 1.381Å. a_0 = 8.93Å.
Quadratic equation: $\sin^2\frac{1}{2}\theta = 0.00743(h^2+k^2+l^2)$, (α-radiation).
$\sin^2\frac{1}{2}\theta = 0.00604(h^2+k^2+l^2)$, (β-radiation).

Finally, we studied the powder-spectrograms of the blood red selenium ultramarine (Guimet) and its corresponding selenium-silver compound. The resulting respective values are here summarized, the intensities following in ( ) the symbols {hkl} of the observed images:

Selenium ultramarine (Guimet).

Images observed: {211} ($\alpha-10$); {310} ($\alpha-4,\beta-1$); {222} ($\alpha-9$); {330}, {411} ($\alpha-8,\beta-1$); {400} ($\alpha-3$); {431}, {510} ($\alpha-8,\beta-1$); {332} ($\alpha-2$); {422} ($\alpha-2$); {433}, {530} ($\alpha-4,\beta-1$); {521} ($\alpha-2$); {440} ($\alpha-4$); {600} ($\alpha-3$); {532}, {611} ($\alpha-3$); {622} ($\alpha-6$); {631} ($\alpha-2$); {444} ($\alpha-3$); {543}, {505}, {710} ($\alpha-3$); {633}, {721} ($\alpha-5$); {642} ($\alpha-1$); {730} ($\alpha-1$); {732} ($\alpha-1$); {800} ($\alpha-1$); {554}, {741}, {811} ($\alpha-1$); {750}, {743}, {831} ($\alpha-1$); {662} ($\alpha-2$); {752} ($\alpha-1$); {840} ($\alpha-2$); {851} ($\alpha-1$); {763} ($\alpha-1$); {844} ($\alpha-1$).
Voltage: 55 K.V.; exposure: 3 hours. $a_0 = 9.10$Å.

Selenium Silver ultramarine.

Images observed: {211} ($\alpha-8$); {310} ($\alpha-7,\beta-1$); {222} ($\alpha-5$); {321} ($\alpha-3$); {330}, {411} ($\alpha-7$); {420} ($\alpha-1$); {332} ($\alpha-1$); {422} ($\alpha-1$); {431}, {510} ($\alpha-2$); {433}, {530} ($\alpha-4,\beta-1$); {440} ($\alpha-3$); {600} ($\alpha-2$); {532}, {611} ($\alpha-3$); {620} ($\alpha-1$); {541} ($\alpha-1$); {622} ($\alpha-2$); {631} ($\alpha-1$); {444} ($\alpha-1$); {543}, {505}, {710} ($\alpha-1$); {633}, {721} ($\alpha-4$); {730} ($\alpha-2$); {732} ($\alpha-3$); {554}, {741}, {811} ($\alpha-1$); {644}, {820} ($\alpha-1$); {622} ($\alpha-2$); {840} ($\alpha-2$); {833} ($\alpha-1$); {655} ($\alpha-1$); {851} ($\alpha-1$); {950} ($\alpha-1$); {666} ($\alpha-2$); {10,3,1} ($\alpha-1$); {774}, {855} ($\alpha-1$); {864}, {10,0,4} ($\alpha-1$).
Voltage: 55 K.V.; exposure: 2 hours. $a_0 = 8.94$Å.

From these data it follows that the substitution of sulphur by selenium, in general, does not influence the structure of the ultramarines to an appreciable degree; the only result is that in the selenium compound the intensity of {222} is greater than {211}, and that of {433} or {530} is greater than {522} or {611}. It also appears that {422} has a somewhat greater intensity than in the sulphur ultramarines, where it is almost as low as zero. The same holds for the selenium-silver compound also; but here it is of interest to find that the intensity of (310) is less than (211)—precisely the opposite to what is found in silver-sulphur ultramarines, and harmonizing with the behavior of the ordinary sodium ultramarines.

Attempts to show a possible connection between the nature of the fundamental silicate of all ultramarines and the silicates of the nephelite or analcite types, gave but negative results.

Nephelite is hexagonal. With the aid of a cylindrical photographic film we secured a rotation-spectrogram having [0001] as the axis of rotation and this gave, for the c-axis direction, a value of 8.38Å. A Bragg-spectrogram on (0001) showed that the spacing in this direction is halved. By means of a rotation-spectrogram having $[10\bar{1}0]$ as the axis of rotation, and by means of a Bragg-spectrogram on $(10\bar{1}0)$ which showed only two images—of the 2d and the 3d order, respectively—we could deduce the cell dimension in the direction of the a axis as = 9.87Å; hence the axial ratio is a:c = 1:0.849, which is in accord with Baumhauer's measurements. Each rhombic cell (= 1/3 of a hexagonal cell) has 8 molecules of $NaAlSiO_4$, so that the total mass included in each triangular prismatic cell amounts to $Na_4Al_4Si_4O_{16}$. The space-group is C_6^6.

In the case of analcite, Bragg-spectrograms on (100) and (211), with rotation-spectrograms in which the crystals (from the Lipari Islands) were rotated on [100], [110] and [111], respectively, showed that the cubic cell had an edge of 13.71Å; and 16 molecules of $NaAlSi_2O_6,H_2O$ are included in it. We determined the space-group as O_h^{10}. It seems possible to assign positions in the structure to all the 120 atoms of the complex molecule $Na_{16}Al_{16}Si_{32}O_{96}$, but this leaves no available space for the 16 H_2O molecules or their constituent atoms. These "mobile" water molecules must then be regarded as "errant" constituents of the structure. This fact will soon be taken up in more detail. According to the above results, neither nephelite nor analcite have anything to do with the constituents of the ultramarines that cause their observed spectra.

We tried to synthesize sodium and potassium aluminosilicates of cubic structure, by melting up together sodium or potassium carbonate and dried kaolin from various localities.[1] In the cases where we used sodium carbonate,

[1] *See also* A. Gorgeu, *Ann. chim. phys.*, (6)10, 169 (1887).

we never succeeded in obtaining cubically crystallizing products, and the spectrograms obtained from them were always identical with those of nephelite. In the case of the potassium salt, however, we could separate from the mass a silicate that crystallized in the cubic system; but its composition did not correspond to the formula $KAlSiO_4$, or a multiple thereof, coming nearer to $K_2Al_2SiO_6$. Roentgen analysis of this product showed that its fundamental lattice is the simple cubic one, with $a_0 = 7.66$Å; and the elementary cell contains the mass $K_6Al_6Si_3O_{18}$. In this case also it is not possible to predicate any relation to the ultramarines. Since the chemical analysis gave no definitive results, however, the question of relationship is not settled.

Our next problem is to deduce the structure of the ultramarines from the results of our spectrographic studies.

At first sight it appears rather certain—as we have seen—that their fundamental grating is a body-centered cubic cell having an edge $a_0 = 9.11$Å. If we take the simplest case, that of nosean ($Na_{10}Al_6Si_6O_{32}S_2$) and consider its structure in the light of our material, we cannot say offhand whether the symmetry is hexakisoctahedral, hexakistetrahedral, or some other. We must, therefore, start by regarding all crystal classes of the cubic system as being, *a priori*, of the same importance.

Since we find all the spacings halved when the sum of the indices in {hkl} is an odd number, there are but ten space-groups to be considered here, namely:[1]

$$T^3;\ T^5;\ T_h^5;\ T_h^7;\ T_d^3;\ T_d^6;\ O^5;\ O^8;\ O_h^9;\ \text{and}\ O_h^{10}.$$

The Bragg-spectrogram on (110) certainly shows the presence of the first-order image of (110), so we may at once drop the T_h^7, T_d^6, and O_h^{10} groups; and as (200) was observed in some cases, O^8 also may be dropped. There remain but six groups, T^3, T^5, T_h^5, T_d^3, O^5 and O_h^9.

These must include $Na_{10}Al_6Si_6O_{32}S_2$ in their elementary cells. Therefore, in order to locate the 6 Si atoms, for example, there must be at least one 6-fold place available in the cell. For this reason we may drop T^5, which has neither 6-fold nor 2-fold places. Since none of the remain-

[1] W. T. Astbury and K. Yardley, *Trans. R. Soc. London*, A224, 254 ff. (1924); R. W. G. Wyckoff, *Carnegie Instit. Wash. Pub.*, 318, 103, 122, 126, 129, 135, 148 (1922).

ing groups possess 4-fold places it is impossible to distribute 6 equal atoms among 2- and 4-fold places. But then arises the trouble that there are but one 2-fold and one 6-fold place available in the groups considered. These two positions have the co-ordinates:

Two-fold position = [000] and $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$

Six-fold position = $[0\frac{1}{2}0]$, $[00\frac{1}{2}]$, $[\frac{1}{2}00]$, $[\frac{1}{2}0\frac{1}{2}]$, $[\frac{1}{2}\frac{1}{2}0]$, and $[0\frac{1}{2}\frac{1}{2}]$ (See Fig. 135).

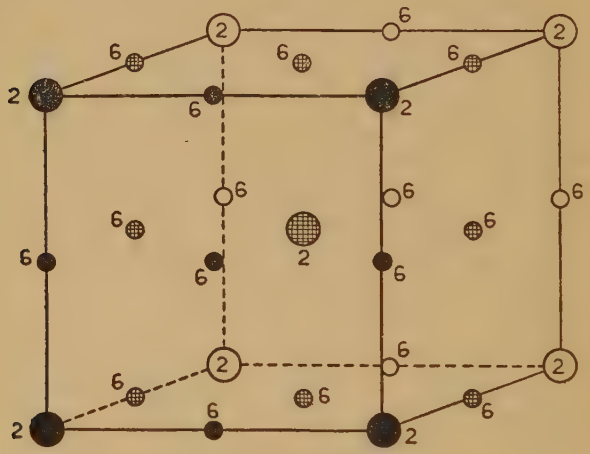


FIG. 135

Moreover, none of these groups have univalent or 4-fold places available. Therefore, if the only available 6-fold place is occupied—say by the six Si atoms—it is already at the start impossible to give six other identical atoms, *e.g.* the six Al atoms, their proper places. It follows that, whatever the special symmetry of nosean may be, there is an appreciable number of its components to which no definite, fixed position can be assigned within the elementary cell. As soon as the six Si atoms are given a place, there is no longer any room at all for the Na, Al, and S atoms—or for the Ca atoms also, in the case of hauyne. The periodic nature of the whole arrangement indicates that these must be "errant" constituents of the structure and without geometrically fixed places. Their influence in the spectrograms must be only a general darkening of the

film or, as in the case with liquids, perhaps giving one or two rings in the vicinity of the central spot.

It may be here remarked that, even if we reject the hypothesis that the lattice is truly the body-centered type, it is still necessary to assume the presence of such "errant" constituents in these structures. This will be found necessary, because there still are too few available positions in the elementary cell to accommodate all the atoms present with fixed positions. It is, therefore, desirable to consider more in detail the possibility of such "errant" constituents, particularly since we have already met an analogous case in analcite where the 16 oxygen atoms of the water molecule could not be accommodated within the elementary cell in places defined by the special symmetry of periodic geometrical arrangement.

The assumption that such errant components are present in crystal structures is not so revolutionary as it seems to be at first sight. In the case of cleveïte and bröggerite, Goldschmidt and Thomassen[1] found that, in all cases, they obtained the spectrographic image of the periodic structure of UO_2 only (by the Roentgenographic method), although the chemical composition of these two minerals is very complicated and variable. They consist chiefly of U_3O_8 with atoms of Pb, Th, Yt, Er, and some molecules of H_2O as accessory components. A certain amount of oxygen present must therefore be distributed at random with the other accessories throughout the pronouncedly periodic UO_2 lattice, which is the only one observed spectrographically. No doubt there is an analogous explanation for the facts that sillimanite and mullite give identical or almost identical Roentgen-spectrograms,[2] as well as for the similar observations concerning a series of Na-Ca-silicates of differing compositions.[3] The same is the case with the "mobile" H_2O molecules in zeolites like analcite; and even more truly than in the cases of nosean and hauyne, does the above apply to the ultramarines. In the latter case we are compelled to assume that many of their "mobile"

[1] V. M. Goldschmidt and L. Thomassen, *Videnskapsselskapets-Skrifter, Kristiania* (1923).
[2] R. W. G. Wyckoff, J. W. Greig, and N. L. Bowen, *Am. J. Sci.*, 11, 459 (1926).
[3] R. W. G. Wyckoff and G. W. Morey, *ibid.*, 12, 419 (1926).

and easily replaceable constituents are errant; and that all these substances have, in addition to their common truly periodic lattice whence comes the identity of their spectrograms, a number of atoms distributed at random.

This assumption explains the particular ease with which some constituents, *e.g.* the Na atoms, can be replaced by others, even under the influence of feeble reactants. Thus even sodium can be replaced by Ca, Sr, Ba, or Pb atoms and our investigations showed that these substitutions are made very readily and very completely, the bivalent metal replacing two Na atoms simultaneously. In this way we obtained almost colorless products whose spectrograms preserved the full character of those of the ordinary ultramarines. Indeed, it is a remarkable fact that two of the Na atoms of a rigorously periodic structure can be thus replaced by one Ca atom without altering the character of the whole structure as revealed by Roentgen-spectrograms. This occurs in the case of the completely isomorphous nosean and hauyne. The concept of errant components within the fundamental structure also explains why Singer and others found intimate relationships between zeolites and permutites on the one hand, and the ultramarines on the other;[1] and the peculiar mode of dehydration of the zeolites—often leaving the original lattice unchanged—which is in such striking contrast to the loss of the water of crystallization by other hydrated salts. The coloring action of the sulphur atoms, which depends on or is intimately related to their dispersion through the lattice, also seems to be closely connected with their errant character.

We had no success in our efforts to determine the true nature of the fundamental silicate common to all these substances and responsible for their identical spectrograms. This led us to try another method for attacking the problem, and we applied it first to the determination of the structure of nosean.

The doubt may arise that the body-centered cubic cell in the fundamental lattice, that is revealed by the spectrographic data, is after all but an apparent one. Perhaps the

[1] F. Singer, *Ueber künstliche Zeolithe.* (Dissertation, Berlin 1911).

special distribution of the atoms in the cell, even though this were not a body-centered one but a simple cubic cell, is equally well able to make the first-order images of {h k l}, if (h+k+l) is odd, so feeble that they could not be detected and therefore would be regarded as having the value zero. If one could find a special arrangement of a complex of Na, Al, Si, O, and S atoms within a simple cubic cell, such that one could calculate an intensity relation congruent with the observed one and at the same time agreeing with the symmetry and other properties of nosean, then such an arrangement might be regarded as a true solution of our problem.

Bragg's recent determinations of the structure of several silicates afford some valuable hints on the way to solve this problem. His results show that in such silicate structures the predominant portion of the frame is composed of the bivalent oxygen ions, which have a fairly constant diameter of 2.66Å for their spheres of action in all these structures. When four such oxygen-spheres are grouped into a regular tetrahedron of contiguous spheres, the distance between the middle points of two opposite edges of the tetrahedron is 4.55Å, or exactly half the dimensions of the cubic cell of nosean, hauyne, and the ultramarines. In nosean 32 O atoms must be grouped within the elementary cell, a number that corresponds exactly to 8 such tetrahedral groups. However, neither the structure of nosean nor that of the ultramarines can correspond to the closest packing of such oxygen atoms: the volume of one oxygen ion in these cases would be about 23.5 cubic Å, while a tetrahedrally-packed oxygen ion is computed to have a volume of only 14 cubic Å. The low refractive index of these minerals (about 1.5 for Na light) also forbids us to assume the closest packing for them. In fact so close a packing would not leave sufficient interstitial space for the Na ions to find places within. On the other hand, it is hardly probable that the 6 Al ions and the 6 Si ions found within each elementary cubic cell would be "errant" constituents. These atoms then must be distributed over either two different 6-fold positions or, less probably, over one 12-fold position—an arrangement that could be

justified by reason of the great functional analogy between aluminum and silicon atoms. We have seen already that there is no possibility of distributing these atoms over two 6-fold positions in any of the space-groups that correspond to a body-centered lattice.

For such an empirical attempt as that mentioned in an earlier paragraph, the space-group O_h^9 and its subgroups O_h^3 and O_2 on the one hand, and the groups T_d^4, T_h^1, and T^1 on the other are perfectly feasible. The O_h^9 group however, corresponds to a body-centered cubic lattice, already found to be unsuited to our purpose; while the other groups correspond to the simple cubic lattice. Among these the group T_d^4 seems to be the most plausible, being also acceptable in the presence of the SO_4 groups of nosean —as soon as one tries to allocate these SO_4 groups hexakistetrahedral is found much more suitable than holohedral symmetry. Moreover, the choice of the O_h^9 group involves—as we have seen—the necessity of distributing the Al and Si atoms over a single 12-fold position;[1] this might be permissible in view of the fact that Al and Si atoms (of 13 and 14 electrons resp.) have very similar diffracting powers, becoming even identical for the ions $Al^{\cdots}$ and $Si^{\cdots\cdot}$, both of which have the configuration of neon. It will soon be apparent, however, that for the calculation of the intensities it makes no great difference whether the SO_4 groups be regarded as having fixed positions, and the agreement with the observed intensities is somewhat better, even, if these ions be considered "errant" ones. In both cases the results are so nearly the same that it is doubtful whether it will ever be possible to choose between the two cases on the basis of the spectrographic results alone. Since the ultramarines do not have a constant Al : Si ratio, there are some indications that Al and Si can actually replace each other isomorphously in these structures, and it is possible that within the whole group of isomorphous ultramarines there may be a transitional series from the body-centered to the simple cubic lattice. This possibility will be considered in more detail later on.

[1] R. W. G. Wyckoff, *The Analytical Expression . . .*, p. 130, 148. The position is 12h in Wyckoff's notation; the only 6-fold place is 6e.

In the space-groups O_h^3 and O_2 the aluminum and the silicon atoms can be distributed between two different 6-fold positions.[1]

In the particular case of nosean we have chosen the space-group T_d^4 as the most probable one.

If two of nosean's sodium atoms be regarded as "errant" ones, then the remaining atoms must be assigned the following coördinates:

To the 8 Na atoms: (uuu), $(\bar{u}u\bar{u})$, $(u+\frac{1}{2}, u+\frac{1}{2}, u+\frac{1}{2})$, $(\frac{1}{2}-u, u+\frac{1}{2}, \frac{1}{2}-u)$, $(u\bar{u}\bar{u})$, $(\bar{u}\bar{u}u)$, $(u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}-u)$, $(\frac{1}{2}-u, \frac{1}{2}-u, u+\frac{1}{2})$.

To the 6 Al atoms: $(0\frac{1}{2}\frac{1}{4})$, $(\frac{1}{4}0\frac{1}{2})$, $(\frac{1}{2}\frac{1}{4}0)$, $(0\frac{1}{2}\frac{3}{4})$, $(\frac{3}{4}0\frac{1}{2})$, $(\frac{1}{2}\frac{3}{4}0)$.

To the 6 Si atoms: $(\frac{1}{2}0\frac{1}{4})$, $(\frac{1}{4}\frac{1}{2}0)$, $(0\frac{1}{4}\frac{1}{2})$, $(\frac{1}{2}0\frac{3}{4})$, $(\frac{3}{4}\frac{1}{2}0)$, $(\frac{3}{4}\frac{1}{2}0)$.

To the 8 O atoms of the (SO_4)-group:

(vvv), $(\bar{v}v\bar{v})$, $(v+\frac{1}{2}, v+\frac{1}{2}, v+\frac{1}{2})$, $(\frac{1}{2}-v, v+\frac{1}{2}, \frac{1}{2}-v)$, $(v\bar{v}\bar{v})$, $(\bar{v}\bar{v}v)$, $(v+\frac{1}{2}, \frac{1}{2}-v, \frac{1}{2}-v)$, $(\frac{1}{2}-v, \frac{1}{2}-v, v+\frac{1}{2})$.

To the 24 O atoms remaining:

(xyz), $(x\bar{y}\bar{z})$, $(\bar{x}y\bar{z})$, $(\bar{x}\bar{y}z)$, $(y+\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2})$, $(\frac{1}{2}-y, x+\frac{1}{2}, \frac{1}{2}-z)$, $(y+\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z)$, $(\frac{1}{2}-y, \frac{1}{2}-x, z+\frac{1}{2})$,

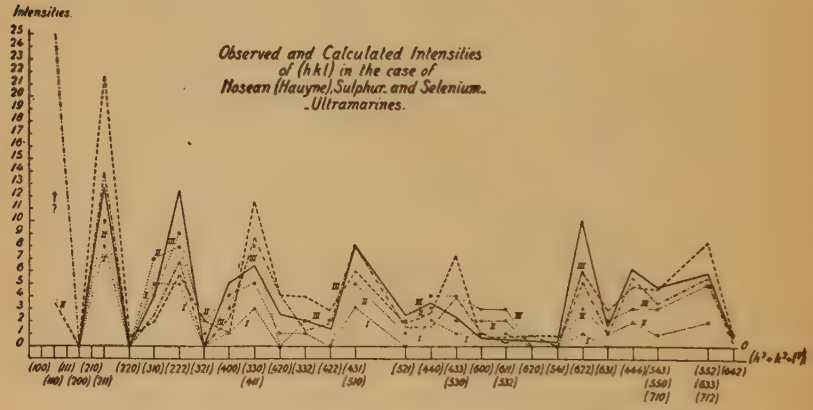
(zxy), $(\bar{z}x\bar{y})$, $(\bar{z}\bar{x}y)$, $(z\bar{x}\bar{y})$, and $(x+\frac{1}{2}, z+\frac{1}{2}, y+\frac{1}{2})$, $(x+\frac{1}{2}, \frac{1}{2}-z, \frac{1}{2}-y)$, $(\frac{1}{2}-x, \frac{1}{2}-z, y+\frac{1}{2})$, $(\frac{1}{2}-x, \frac{1}{2}+z, \frac{1}{2}-y)$,

(yzx), $(\bar{y}zx)$, $(y\bar{z}\bar{x})$, $(\bar{y}z\bar{x})$, $(z+\frac{1}{2}, y+\frac{1}{2}, x+\frac{1}{2})$, $(\frac{1}{2}-z, \frac{1}{2}-y, x+\frac{1}{2})$, $(\frac{1}{2}-z, y+\frac{1}{2}, \frac{1}{2}-x)$, $(z+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-x)$.

In these formulas the parameters must be chosen as follows: u = 0.250; v = 0.103; x = 0; y = z = 0.354. The value u = 0.250 cancels the difference in the calculation for the sodium atom in case we use either O_h^3 or T_d^4. The calculated and observed intensities of nosean, hauyne, and of a number of sulphur and selenium ultramarines are presented in Figure 136. The drawing gives the calculated intensities for both the "fixed"-structure component ($Na_8Al_6Si_6O_{24}$) alone, regarded as composed of "atoms" (solid line), and as a structure of "ions" (dotted line). It also presents the intensities for the case where the SO_4 groups have been assigned "fixed" positions (dot-and-dash line). The dotted lines I, II, and III, represent the intensities for nosean and the ultramarines. There is very satisfactory agreement between the calculated and the observed values. The question as to whether the "fixed" constituent

[1] *Ibidem*, p. 133, 139; positions 6f and 6g in Wyckoff's notation.

is present in the form of "atoms" or "ions", cannot be definitely answered; the differences are but slight in both cases and the observed intensities are too roughly estimated to permit a final decision. The volumes of the spheres of action used make it highly probable, however, that "ions" are the real building stones of the whole structure. I would here repeat that the component ($Na_8Al_6Si_6O_{24}$) can be equally well arranged upon the basis of O_h^3 and its geometrical subgroups O_2, T_d^4, T_h', and T_1; but that as soon


Intensities.
Observed and Calculated Intensities of (hkl) in the case of Nosean (Hauyne), Sulphur- and Selenium-Ultramarines.

..... Observed intensities: . S-ultramarine (II) ₒ Se-ultramarine (III) x Nosean (I) and Hauyne;—fixed radical (atomic) ·—·—·— fixed radical (ionic) – – – – fixed radical, $2SO_4''$ in Nosean (ionic).

FIG. 136

as the SO_4 groups of nosean are assigned "fixed" positions, then a holohedral symmetry cannot be sustained and the hexakistetrahedral group T_d^4 becomes the most probable one.

In a rigorously periodic structure the Na_2SO_4 of nosean and hauyne cannot be replaced by $CaSO_4$, nor in the ultramarines by Na_2S_2, Na_2S_3, and the like. This alone makes it necessary, *a priori*, to abandon the supposition of a rigorously geometrical arrangement of these constituents within the framework of the crystals; for this reason, also, the conclusion is inevitable, that "errant" constituents are present in the framework.

The deduced structure of the "fixed" component ($Na_8Al_6Si_6O_{24}$) is represented in part by Figure 137. This figure, which represents a projection of the cell on (001), has the oxygen atoms as large spheres; the other spheres are of their proper sizes. In the actual structure, however, if the $Si^{\cdots}$, $Al^{\cdots}$ and S^{VI} ions are to be contained by the

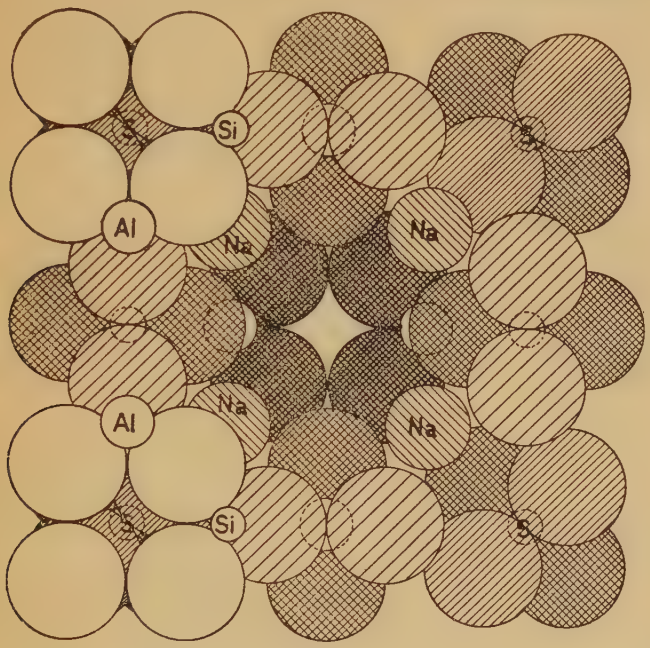


FIG. 137

oxygen-tetrahedra without distorting the structure, the ionic diameters must be reduced to about 0.58Å. The right-hand side of the figured cell is built up to one-fourth of its height, and the left-hand side about half, so that only the portion beneath and within a plane (012) is represented there. For the sake of clearness the SO_4 group in the center of the cell has been omitted.

There are two cases to be considered here: (*a*) the only "fixed" constituent of the structure is the radical $(Na_8Al_6Si_6O_{24})^{\cdot\cdot}$ and (*b*) a fixed place has been assigned to the SO_4 groups of nosean.

(*a*) The only "fixed" component is $(Na_8Al_6Si_6O_{24})^{\cdot\cdot}$, the remaining atoms being "errant" ones (Fig. 136, solid line). It appears that each lateral face of the elementary cell contains two Al ions and two Si ions, each surrounded tetrahedrally by four O ions. Each of these ions has the proper S^4-symmetry in the space-group in T_d^4, or V_d in the space-group O_h^3.

Also it appears that 8 Na ions are situated on the diagonals of the cubic cell at 1/4 and 3/4 of their lengths. Each sodium ion has the proper symmetry—D_3 in T_d^4 and T_h^1, and C_3 in T^1—and is surrounded by 6 O atoms at a distance of 2.64 Å.[1] The sodium atoms are located in the great cavity (=2.66Å) between these six O atoms and therefore have plenty of room to move about freely. Thus it is easily possible to replace them by $Li^{\cdot}$, $K^{\cdot}$, $Ag^{\cdot}$, $Tl^{\cdot}$ and $(NH_4)^{\cdot}$ ions, whose diameters are even smaller, or of analogous size.[2] It is less easy to substitute $Rb^{\cdot}$ ions and still less so the $Cs^{\cdot}$ ions, and these conditions were actually reflected by the speeds observed in our syntheses of the different ultramarines and in those by means of the silver ultramarines. It is this mobility of the Na ions within these cavities, that gives rise to the replaceability of the alkali atoms in the minerals we are studying, when the latter are placed in contact with solutions containing ions of other alkali metals. It is now also possible to understand why the even smaller ions of the bivalent metals Zn, Mn, and Ca are so readily and completely substituted in these compounds. Perhaps this phenomenon is fundamentally connected with the selective absorption of the soil, a large proportion of which contains permutite-like zeolitic silicates; and also with the stimulation to plant growth produced by traces of zinc and manganese (Bertrand), as well as the predominant rôle of calcium.

It is also to be noted that the center of the elementary cell is a large cubical cavity having an edge of 3.7 Å and six cross-wise extensions of the same. In this cavity there is more than enough room for such electrically charged groups as $NaSO_4'$, NaS_3', or $(Na,Ca)SO_4'$, or for elemental ions S'', $Na^{\cdot}$, and the like. There and in the corners of

[1] In T^1 they are distributed among two groups of 4 atoms each. It is impossible to place 6 of the 8 Na ions in the centers of the lateral faces and middle of the cube edge (Fig. 135), unless we drop the assumed tetrahedral arrangement of the O atoms. The open space at these points is not more than 0.54 Å, which is too small for the sodium atom of 1.98 Å diameter.

[2] Radii of the ions used are (in Å units):

$Li^{\cdot}$	= 0.79	$Rb^{\cdot}$	= 1.49	$Zn^{\cdot\cdot}$	= 0.83
$Na^{\cdot}$	= 0.99	$Cs^{\cdot}$	= 1.65	$Ca^{\cdot\cdot}$	= 1.06
$K^{\cdot}$	= 1.33	$Tl^{\cdot}$	= 1.49	$Sr^{\cdot\cdot}$	= 1.27
		$Ag^{\cdot}$	= 1.13	$Ba^{\cdot\cdot}$	= 1.42
				O''	= 1.33
$Mg^{\cdot\cdot}$	= 0.78	$Al^{\cdot\cdot\cdot}$	= 0.57		
$Hg^{\cdot\cdot}$	= 1.12	$Si^{\cdot\cdot\cdot\cdot}$	= 0.29		
$Pb^{\cdot\cdot}$	= 1.32	S^{VI}	= 0.24		
$Mn^{\cdot\cdot}$	= 0.91				

For $Al^{\cdot\cdot\cdot}$, $Si^{\cdot\cdot\cdot\cdot}$ and S^{VI}, the contractions mentioned above are to be applied in Fig. 137.

the cell, the errant constituents find space to dwell and to move freely. These spaces for freely moving constituents also may take up water or solutions, and their presence explains the remarkable hydraulic properties and the general absorption phenomena of the ultramarines and permutites, reminding one strongly of the behavior of colloidal systems. The electrical charges on the walls of such cavities may help to fix the electrically charged ions, or to render the finely divided powders strongly "active".

There appears to be no true "mother-silicate" in either these minerals or in the ultramarines. The effort to separate it out is as idle as that of isolating the ammonium ion from the ammonium salts. There seems to be nothing but a certain electrically charged radical present, in our case this is $(Na_8Al_6Si_6O_{24})\cdot\cdot$, and it is very probable that, for instance in nosean, the remaining two errant sodium atoms, or sodium ions, will be even more readily replaced by other ions—mobile as they evidently are—than were the six other ones. It will not be possible to detect the influence of this substitution on the spectrograms, however, until that substitution has progressed to the sodium atoms of the fixed radical. In fact a change in the character of the ultramarine spectrogram[1] and its gradual change into that of the silver ultramarine, could not be detected by us until after about 12 to 18 per cent of silver had already entered into the sodium ultramarine.

(*b*) A *fixed* place assigned to the SO_4 groups of nosean, only two sodium atoms being errant ones.

This was the assumed case in the previous calculations of the different intensities of nosean. The SO_4 groups then must be inserted in the eight corners and the center of the space of the elementary cell, as indicated by Figure 137. The four O atoms also are arranged in tetrahedra that must be placed accurately with respect to the other constituents, *i.e.* into the diagonals of the cube and contiguous to the sodium atoms. Now the symmetry can no longer be O_h^3, but must be reduced to T_d^4, O_2, T_h^1, or T^1. In the groups T_d^4 and T^1, the ternary axes are heteropolar; the diagonals of the cubic cell are therefore occupied by atoms in such a manner that a sodium atom located on them is always between two subsequent sulphur atoms at the points [ooo] and $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$; each sodium atom being either next to the top or to the basal face of the subsequent oxygen-tetrahedron surrounding each sulphur atom. The distances from the sodium atoms to the tops or the basal faces of these subsequent oxygen-tetrahedra are usually unequal. In the space-group T_d^4 the sodium atom has, moreover, one degree of freedom since its parameter is u, and may be shifted along the cube's diagonal in either direction. If perchance *u* for the sodium atom has attained a value such that the atom is exactly between the two subsequent sulphur-atoms, then its distance from the adjacent oxygen atom is 2.30 Å—

[1] Nosean has only two errant sodium atoms, but in the ultramarines there must be more among their constituent atoms. In the silica-poor ultramarines of low sulphurization, only the S_2 could possibly find a fixed position in the structure; in the mixtures of higher sulphurization, S_3, S_4, etc., these sulphur atoms and the excess alkali atoms must be errant.

a value in perfect agreement with the sum of the radii of a $Na^{\cdot}$ and an O'' ion (*i.e.* 0.99 + 1.33 = 2.32 Å).

In the space-group T_h^1 the ternary axes are homopolar, however, and therefore the subsequent oxygen-tetrahedra must be arranged alternately in opposite manners along the cube diagonals. Thus the sodium atoms would lie either between the summits or the bases of each pair of subsequent oxygen-tetrahedra. This arrangement is not a very probable one because then the intensities of faces (hkl), h+k+l being odd, would still have an appreciable value which does not agree with experimental results.

Industry recognizes two kinds of ultramarines: those poor in silica and having an atomic ratio Al : Si closely equal to 1 : 1 ; and those rich in silica and having the ratio Al : Si about 1 : 1.5.

Experiment shows, however, that:

a. all chemical analyses of the ultramarines give variable results and are in but approximate agreement with certain stoichiometric formulas;

b. all the powder-spectrograms are identical, whether they are for those ultramarines poor in silica or for the silica-rich ones;

c. all technical ultramarines, on decantation, yield fractions of slightly different molecular weight. On account of their highly inconvenient hydraulic properties, however, which make them behave like paste-forming materials, it is practically impossible to sort them into well-defined fractions.

These facts cause one to suspect that all the technical products are really mixtures of isomorphous, and analogously constituted substances; and that that is the reason for the identical Roentgen-patterns on the one hand and the inconstant analytical results on the other.

From considerations discussed above, it seems that in the probable structure of these compounds, the sum of the aluminum and the silicon atoms equals twelve. The diffractive powers of both kinds of atoms is, as usual with them, very slightly different and becomes zero for the $Al^{\cdot\cdot\cdot}$ and the $Si^{\cdot\cdot\cdot\cdot}$ ions themselves. This is the reason why ultramarines having the places of one or more aluminum atoms occupied by a silicon atom, yield diffraction-patterns practically identical with those obtained from

ultramarines in which all 6 aluminum atoms are present as well as the 6 silicon atoms. For example, ultramarine having the "fixed" radical $(Na_8Al_5Si_7O_{24})\cdots$ and $(Na_8Al_4Si_8O_{24})\cdots\cdot$ give spectrograms that are practically identical with those having the radical $(Na_8Al_6Si_6O_{24})\cdot\cdot$. It must be evident, however, that mixtures of such ultramarines, when in the proper ratio, will yield empirical compositions that may closely approach that of a hypothetical "compound" in which Al : Si = 1 : 1.5. For instance, if two "molecules" of an ultramarine having $(Na_8Al_4Si_8O_{24})\cdots\cdot$ as its fixed component be mixed with one molecule of an ultramarine with the fixed radical $(Na_8Al_6Si_6O_{24})\cdot\cdot$, the resulting mixture will appear to have the composition corresponding to one molecule of an ultramarine with a radical $(Na_8Al_{4.6}Si_{7.3}O_{24})$ where the ratio Al : Si is about 1 : 1.57. It is quite possible that such substitutions may lower the symmetry of the whole structure and change it to some other one of the space-groups we have considered. Here also, however, this fact will hardly be revealed by a study of their spectrograms and their relative intensities. On calculating the intensities we found that, also in the case where 8 Na atoms of the fixed radical are replaced by 4 tetrahedrally arranged Na atoms, the curve of relative intensities is changed but slightly. Even in this case there is a close agreement between the calculated and the observed intensities. This also explains the identity of the spectrograms in the case where there are less than 8 Na atoms present in the blue ultramarines.

It must be evident that it is quite futile to attribute definite "chemical formulas" to the technical ultramarines, or to give a stoichiometric interpretation to their chemical analyses. The Roentgen-spectrograms remain practically the same, also, if such errant constituents as NaS_2', NaS_3', NaS_4' and the like, are replaced by others. In this respect the general properties of the ultramarines are sufficiently explained as resulting from the predominant influence of their "fixed" radical.

In conclusion, we may consider briefly the cause of the colors of these remarkable substances, a phenomenon long a puzzle to chemists and still a mysterious one.

Their colors range from a very intense dark blue, through the pale blue of some silica-poor and sulphur-poor specimens, to yellow, green, pink, and red, up to violet. The similarity in composition, in spite of the great differences in color, has gradually convinced chemists that the actual coloring matter forms but a very small proportion of their total mass. In this case, then, the coloring matter must be distributed throughout the whole crystal structure of the particles making up these remarkable sulphosilicates.

The sulphur present in the ultramarine undoubtedly has predominant significance for the color. The color becomes deeper and more intense as the sulphurization increases. The special nature of the alkali and other metallic constituents, however, must play an important part in the phenomenon of color: lithium and thallium ultramarines are darker and have a warm violet hue; calcium and zinc ultramarines are colorless or nearly so; silver ultramarines are yellow or grayish. Ultramarines rich in silica generally have a warmer glow than the silica-poor ones. If the sulphur is replaced by selenium, the color becomes blood red; if it is replaced by tellurium the mass turns to a yellow. Knapp, Hoffmann, and others demonstrated that boron can replace all the silicon and all the aluminum in the ultramarines. In 1910 Hoffmann pointed out that, in the silica-free boron ultramarines obtained by him, the boron content corresponds exactly to the total silicon+aluminum content.[1] It appears, therefore, that boron replaces not only the chemically congenial aluminum, but the silicon atoms at the same time. This fact again illustrates the close relationship between the functions of these two elements as ions in the ultramarines.

On the other hand, starting with sodium aluminate alone, it is impossible to obtain colored products from reactions with sulphur or sulphides. If one heats the boron-

[1] J. Hoffmann, *Chem. Ztschr.*, 34, 821 (1910); F. Knapp, *Dinglers polytech. J.*, 233, 479 (1879).

ultramarine at the proper temperature, no color is developed until a certain excess of boric acid has been added to the molten mass of borax and sodium sulphide. It seems that the mass must first attain a certain mobility—a sufficient amount of the acid reducing its viscosity—before favorable conditions for the dispersion and dissemination of the coloring agent throughout the mass can be realized. One gets the impression that the medium in which the sulphur or its special compound is dissolved, must attain certain physical conditions before the coloration phenomenon can set in.

We know a number of cases where molten sulphur compounds acquire a blue color at high temperatures, losing it when the mass cools. Evidently in these cases the phenomenon of color is based on a reversible process. Molten KCNS, for example, if heated above a certain temperature shows a blue color that gradually disappears as the liquid cools. It seems reasonable to suppose that here the phenomenon is connected with a reversible transformation—whether it is a dissociation of the form $KCNS \rightleftarrows KCN + S$, or a dislocation, $KCNS \rightleftarrows KCN.....S$ —where the sulphur atom is deformed and is brought into a special state of electronic configuration determined by the nature of the other complexes of atoms from which the sulphur atom has been more or less removed. Several investigators have shown that sulphur atoms are specially adapted to show such coloring phenomena under conditions of total or partial dissociation from their original molecules.[1] In fact, mere traces of such substances are sufficient to produce intense colorations, as is well known. Gold-glass is an excellent example of this fact; for in its preparation only one part of gold is mixed with 1000, 10,000, or even 20,000 parts of the silicate, which latter actually takes up even much less than this proportion of the gold during the process. Here also the original product is colorless but becomes intensely red after it is kept at a

[1] P. von Weimarn, *Kolloidchem. Beihefte*, **22**, 38 (1926); Wo. Ostwald, *ibidem*, **2**, 409 (1911); J. Hoffmann, *Kolloid-Z.*, **10**, 275 (1912); Paterno and Mazzuchelli, *Atti accad. Lincei*, (5) **16-i**, 465 (1907); Wo. Ostwald and Auerbach. *Kolloid-Z.*, **38**, 336 (1925).

higher temperature, below its melting point, for a long time. A somewhat analogous phenomenon is known in ceramics, in the case of the so-called "pinks", *i.e.* mixtures of stannic acid, SnO_2, calcium carbonate and a small amount of chromium trioxide, which develop a red or lilac color on melting the mixture up with an excess of a boron silicate glass.

In the case of the pigment of such ultramarines as lapis lazuli, the sulphur atoms cannot have "fixed" positions in the structure, as we have seen; they are errant constituents, either atoms or ions, within the large spaces in the center and the corners of each elementary cell. Sodium atoms also may be errant within these cavities, and it is not unlikely that in many cases there are formed ions of the types NaS_2', NaS_3', and NaS_4', that are more or less dislocated or probably even dissociated by their mutual collisions due to their free mobility within the great cavities. Such circumstances would be very similar to those depending on temperature only, as described above for KCNS. As these collisions become more numerous with increasing concentration of the sulphur ions one can, perhaps, understand why the blue color of the ultramarines deepens as the degree of sulphurization increases. These cavities being surrounded by walls of electrically-charged atoms of the "fixed" constituents, it seems quite probable that the electromagnetic conditions within the cavities may be highly favorable for bringing the errant sulphur and sodium atoms they inclose, into precisely that state of deformation required for the appearance of the selective photo-absorption that causes the coloration phenomena. The permanent color of the ultramarines, in contrast to the unstable color of molten KCNS, is precisely because of the continuous collisions of the freely moving sulphur atoms in the former.

Undoubtedly there remains much work to be done before the puzzle of the ultramarines may be considered to be completely solved. In particular, systematic analytical research must furnish us much more certain information

regarding the manner in which substitutions take place under known concentration, time, and temperature conditions. This must be supplemented by complementary calculations of the intensities of the diffraction-images of the powder-spectrograms in cases where definitely-known amounts of Na, Ag, Ca, Th, and other components have replaced sodium atoms. I think, however, that the solution of the problem of the ultramarines has been brought much nearer to attainment by the investigations summarized in this Section.

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